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THE JOURNAL

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THE AMERICAN CERAMIC SOCIETY

Vol. 26 July 1, 1943 No. 7

EFFECT OF OPACIFIERS ON FUSED VISCOSITY OF FELDSPATHIC GLAZES*

By James R. Beam

Abstract

A study has been made of the fusion characteristics of feldspar, flint, kaolin, and whiting used in glaze compositions with zinc oxide and various opacifiers. The fusion characteristics of tin oxide, Opax, Zircopax, and various combinations of opacifiers are given. All heat-treatments mentioned are at cone 12. Isoviscosity triaxial diagrams show the fields of good glazes in each series, and the relative effects of composition changes on the physical properties are outlined.

I. Introduction

The purpose of this study was to reduce to tabular form the scattered knowledge of the fusion characteristics of simple one-fire glaze compositions and to designate those fields worthy of further consideration. All of the heat-treatments referred to have been obtained at cone 12 in a commercial tunnel-kiln firing on a 52-hour cycle.

II. Review of Literature

Since the work of Seger[1] on heat-measurement compositions, there have been many investigations on the varying relations of feldspar, flint, kaolin, and whiting with zinc oxide and various opacifiers. Few of the writers, however, mention the relative fusion characteristics and their relation to common glazes.

The general characteristics of the effect of various changes in the chemical composition of porcelain glazes have been ably presented by Purdy.[2] The basic study of glazes of this type has been outlined by Watts[3] and by Hanna,[4] and their work has been useful in determining the background of this investigation. Minton[5] has also discussed the effect of several opacifiers. Some of the fusion characteristics of porcelain glazes have been outlined by Sortwell,[6] showing the fields of good two-fire glazes using constant RO, alumina, and silica as the end members of triaxial diagrams. Additional information has been given by Twells.[7]

III. Methods of Measuring Fused Viscosity

The ordinary methods of measuring "fused viscosity of glasses" do not apply to glazes because of their higher viscosity. The "dropping" or "oscillating ball" methods and the "rotating cylinder" method outlined by Morey[8] are not applicable to glazes because of the vast differences in the thicknesses being measured. Such glass technique conceptions as the rate at which gas bubbles rise through the fused mixture, however, do apply to glazes and to the final texture of the glaze.

The viscosity of the more viscous ceramic mixtures, such as those outlined in investigations on the viscosity of porcelain bodies by Bleininger and Kinnison[9] likewise do not apply to glazes. The fused viscosity of a glaze lies between the extremes of a glass technique and that of porcelain.

One-fire glazes must be regarded as mixtures of the glaze constituents plus that portion of the body that has reacted with the glaze constituents. The natural effect of the body is to satisfy deficiencies in the ratio of

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 23, 1942 (White Wares Division). Received January 25, 1943.

[1] Hermann A. Seger, Collected Writings, Vol. I, pp. 230–49. American ed., edited by A. V. Bleininger, Chemical Publishing Co., Easton, Pa., 1902.

[2] R. C. Purdy, "Porcelain Glazes," *Trans. Amer. Ceram. Soc.*, **13**, 550–84 (1911).

[3] A. S. Watts, "Study of Bristol Glazes Compounded on the Eutectic Basis," *ibid.*, **18**, 631–41 (1916).

[4] H. H. Hanna, "Study of the Most Fusible Mixtures of K_2O, CaO, Al_2O_3, and SiO_2," *ibid.*, **17**, 672–90 (1915).

[5] R. H. Minton, "Use of Substitutes for Tin Oxide in Glazes," *Jour. Amer. Ceram. Soc.*, **3** [1] 6–12 (1920).

[6] H. H. Sortwell, "High-Fire Porcelain Glazes," *ibid.*, **4** [9] 718–30 (1921).

[7] (*a*) Robert Twells, Jr., "Field of Porcelain Glazes Maturing Between Cones 17 and 20," *ibid.*, **5** [7] 430–39 (1922).

(*b*) Robert Twells, Jr., "Further Studies of Porcelain Glazes Maturing at High Temperatures," *ibid.*, **6** [11] 1113–27 (1923).

[8] G. W. Morey, Properties of Glass, pp. 135–72. Amer. Chem. Soc. Monograph Series, Reinhold Publishing Co., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48 (1939).

[9] A. V. Bleininger and C. S. Kinnison, "Viscosity of Porcelain Bodies," *Trans Amer. Ceram. Soc.*, **17**, 130–36 (1915).

alumina to silica of the glaze and also to broaden the range of the glaze. This condition is marked in vitrified one-fire porcelains.

IV. Procedure

It is common practice to measure time-temperature relations of ceramic fusions by what is known as "cone deformation," which occurs as a result of a definite viscous flow. Cone deformation, however, can be used only with mixtures sufficiently refractory to retain some resemblance to the original cone. A greater amount of deformation takes place in glazes, and the test must be modified to accommodate a glaze with considerable flow. The "cone deformation" method and the method described in this paper measure the results of a viscous flow and therein differ from the usual conception of viscosity.

The viscosity trials were made by molding carefully the dry powdered material in a brass conical mold, $1^1/_2$ in. in diameter at the base and $1^3/_4$ in. high. All cones were made from dry powder with no adhesive or bonding agent added. The cone was transferred to an unfired clay disk made from casting slip being used in production. Considerable care was necessary to develop the proper technique of transferring the formed powder cone to the tile without distorting the cone.

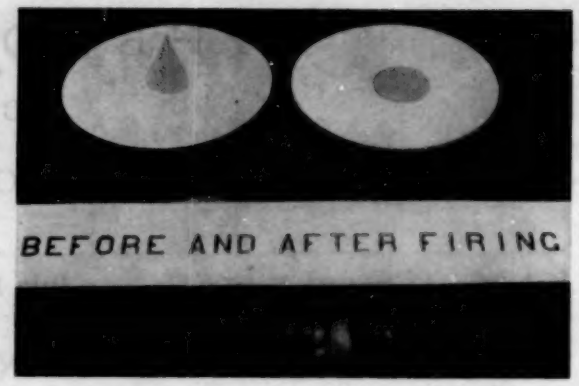

FIG. 1.—View of cones before and after firing.

The area of the fused mass, which was determined with a planimeter, could be taken as a measure of the fused viscosity to obtain the relative fusion character of the various compositions. The trials reported in this paper, however, were sufficiently uniform to justify using the diameter of the fused mass as the measure of the fused viscosity. All viscosity factors are reported as the diameter of fused trials measured in millimeters. Figure 1 shows a view of the cones before and after

TABLE I

CALCULATED CHEMICAL COMPOSITION OF TEST GLAZES

Composition (%) of basic series containing feldspar, flint, kaolin, and whiting

Series No. 1 A

Member No.	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Viscosity factors
1	82.11	8.80	5.40	0.05	2.99	0.52	29.5
2	80.43	9.75	5.41	0.05	3.59	0.62	31.4
3	78.75	10.71	5.44	0.05	4.19	0.72	36.8
4	77.08	11.68	5.45	0.05	4.79	0.82	38.5
5	75.40	12.62	5.48	0.05	5.39	0.93	39.2
6	73.72	13.58	5.50	0.05	5.98	1.04	39.2
7	72.06	14.54	5.51	0.05	6.58	1.13	40.5
8	70.38	15.49	5.53	0.05	7.17	1.24	41.0
11	80.75	8.01	8.21	0.04	2.45	0.42	29.5
12	79.02	8.98	8.23	0.05	3.06	0.53	32.6
13	77.31	9.95	8.24	0.05	3.67	0.64	41.8
14*	75.59	10.94	8.27	0.05	4.28	0.74	43.0
15*	73.88	11.92	8.28	0.05	4.89	0.84	42.5
16	72.17	12.88	8.31	0.05	5.50	0.95	44.7
17	70.46	13.86	8.33	0.05	6.11	1.06	44.2
18	68.76	14.84	8.34	0.05	6.72	1.16	43.7
21	79.30	7.20	11.13	0.05	1.89	0.32	30.2
22	77.56	8.19	11.15	0.06	2.51	0.43	36.8
23	75.79	9.19	11.17	0.07	3.13	0.54	45.6
24*	74.04	10.19	11.18	0.07	3.75	0.65	47.5
25*	72.28	11.19	11.21	0.07	4.37	0.75	47.0
26*	70.54	12.19	11.23	0.07	4.99	0.86	48.3
27	68.79	13.17	11.25	0.07	5.63	0.97	48.5
28	67.04	14.17	11.27	0.07	6.24	1.08	48.3
32	76.01	7.33	14.21	0.07	1.93	0.33	29.8
33	74.21	8.34	14.24	0.07	2.56	0.44	35.0
34	72.41	9.37	14.25	0.08	3.19	0.55	49.0
35*	70.63	10.38	14.26	0.08	3.84	0.67	49.9
36*	68.83	11.41	14.30	0.08	4.47	0.00	52.1
37	67.05	12.43	14.31	0.08	5.11	0.88	53.7
38	65.26	13.43	14.34	0.08	5.75	0.99	53.6
43	72.56	7.48	17.43	0.09	1.97	0.33	31.8
44	70.72	8.53	17.45	0.09	2.62	0.45	42.3
45	68.88	9.57	17.45	0.10	3.27	0.57	46.1
46*	67.06	10.60	17.47	0.10	3.92	0.68	49.2
47	65.22	11.65	17.51	0.10	4.57	0.78	53.0
48	63.40	12.69	17.52	0.10	5.22	0.90	54.1
49	61.56	13.77	17.55	0.10	5.88	1.02	59.4
54	68.95	7.69	20.79	0.09	2.02	0.34	36.5
55	67.08	8.75	20.82	0.09	2.68	0.46	43.3
56	65.20	9.82	20.83	0.10	3.34	0.58	46.6
57	63.34	10.87	20.84	0.10	4.01	0.70	47.9
58	61.45	11.95	20.88	0.10	4.68	0.80	50.1
59	59.58	13.02	20.90	0.10	5.34	0.92	55.6

* Compositions within the good glaze field at cone 12.

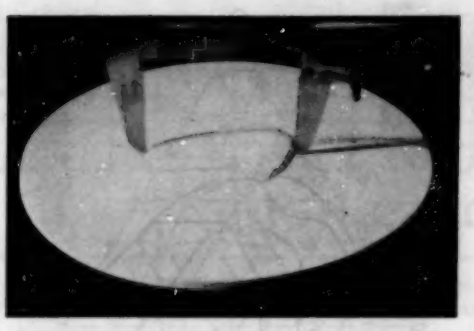

FIG. 2.—Viscosity measurement of fired cones with caliper.

firing. Figure 2 shows how the viscosity is measured by calipering the diameter of the fired cone.

In preparing the test samples, each member was calculated and made up as small straight-line series to minimize blending errors. All samples were ground in a ball mill, and two or more unfired round tile cast from regular production casting slip were sprayed with each member and fired with the fused cone samples.

All glaze compositions were made of commercial ceramic raw materials. The calculated chemical compositions are given in Table I to permit an interpretation of the results in terms of the other materials. The resulting viscosity factors have been plotted as "isoviscosity" lines on the original composition triaxials in order to show the conclusions of this investigation. The glaze compositions of any given viscosity factor may be read directly from the diagrams, which are convenient for determining the necessary changes in composition for any desired change in the fused viscosity. The area of good glazes at cone 12 is inclosed with a black line on the diagrams.

It is interesting to note the range of the good glaze

TABLE I (*concluded*)

Glazes containing feldspar, flint, kaolin, whiting, tin oxide, and zinc oxide (%)

Member No.	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	ZnO	SnO_2	Viscosity factors
				Series No. 1 B					
14	71.07	10.29	7.78	0.05	4.02	0.69		6.10	42.8
24	69.52	9.56	10.50	0.06	3.52	0.61		6.22	45.4
25	67.87	10.51	10.53	0.06	4.11	0.70		6.22	46.1
26	66.23	11.44	10.54	0.06	4.69	0.81		6.22	46.8
35	66.25	9.73	13.37	0.07	3.60	0.62		6.35	48.7
36	64.55	10.70	13.41	0.07	4.19	0.72		6.35	49.8
				Series No. 3 B					
25	65.16	10.09	10.11	0.06	3.94	0.68	3.98	5.97	54.0
35	63.55	9.34	12.83	0.07	3.45	0.60	4.06	6.09	56.7
46	60.21	9.52	15.68	0.09	3.52	0.61	4.14	6.22	56.7
56	58.38	8.79	18.65	0.09	2.09	0.52	4.23	6.35	58.2
				Series No. 4 B					
26	62.35	10.77	9.92	0.06	4.41	0.76	5.86	5.86	55.8
27	60.80	11.64	9.94	0.06	4.97	0.86	5.86	5.86	56.4
28	59.25	12.52	9.96	0.06	5.52	0.96	5.86	5.86	57.5
29	57.71	13.42	9.98	0.06	6.07	1.04	5.86	5.86	63.7
36	60.69	10.06	12.61	0.07	3.94	0.68	5.97	5.97	59.5
37	59.12	10.96	12.62	0.07	4.50	0.78	5.98	5.98	60.2
38	57.54	11.84	12.64	0.07	5.07	0.88	5.98	5.98	62.5
39	55.96	12.75	12.66	0.07	5.63	0.98	5.98	5.98	65.0
46	58.99	9.33	15.36	0.09	3.45	0.60	6.09	6.09	61.2
47	57.36	10.25	15.40	0.09	4.02	0.69	6.09	6.09	62.2
48	55.76	11.16	15.41	0.09	4.59	0.79	6.09	6.09	63.1
49	54.12	12.11	15.43	0.09	5.17	0.89	6.09	6.09	65.0
				Series No. 5 B					
26	61.15	10.57	9.73	0.06	4.33	0.75	7.66	5.75	58.0
27	59.63	11.42	9.75	0.06	4.88	0.84	7.66	5.75	59.9
28	58.12	12.28	9.77	0.06	5.41	0.94	7.66	5.75	61.8
36	59.51	9.86	12.36	0.07	3.87	0.66	7.81	5.86	62.3
37	57.97	10.74	12.37	0.07	4.41	0.76	7.81	5.86	64.7
38	56.42	11.61	12.39	0.07	4.97	0.86	7.81	5.86	64.0
46	57.82	9.14	15.06	0.09	3.38	0.59	7.96	5.97	60.0
47	56.22	10.04	15.09	0.09	3.94	0.68	7.96	5.97	64.4
48	54.65	10.94	15.10	0.09	4.50	0.78	7.96	5.97	65.3
49	53.04	11.86	15.12	0.09	5.07	0.87	7.96	5.97	67.9

Glazes containing feldspar, flint kaolin, whiting, and Zircopax (%)

Member No.	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	ZrO_2	Viscosity factors
				Series No. 1 D				
15	70.42	10.95	7.56	0.05	4.46	0.77	5.78	44.5
16	68.85	11.83	7.58	0.05	5.03	0.87	5.79	45.3
24	70.49	9.35	10.19	0.06	3.42	0.59	5.89	40.8
25	68.89	10.27	10.22	0.06	3.98	0.68	5.90	43.0
26	67.30	11.17	10.23	0.06	4.55	0.78	5.90	43.1
27	65.70	12.07	10.25	0.06	5.12	0.89	5.90	43.0
35	67.33	9.51	12.97	0.07	3.49	0.60	6.01	42.7
36	65.69	10.44	13.00	0.07	4.07	0.70	6.02	43.1
37	64.07	11.37	13.02	0.07	4.64	0.80	6.02	44.3

Glazes containing feldspar, flint, kaolin, whiting, and Opax (%)

				Series No. 1 E				
14	69.68	10.02	7.55	0.05	3.91	0.79	7.99	42.4
15	68.12	10.91	7.57	0.05	4.46	0.89	7.99	44.6
26	64.96	11.14	10.23	0.06	4.55	0.91	8.15	47.8

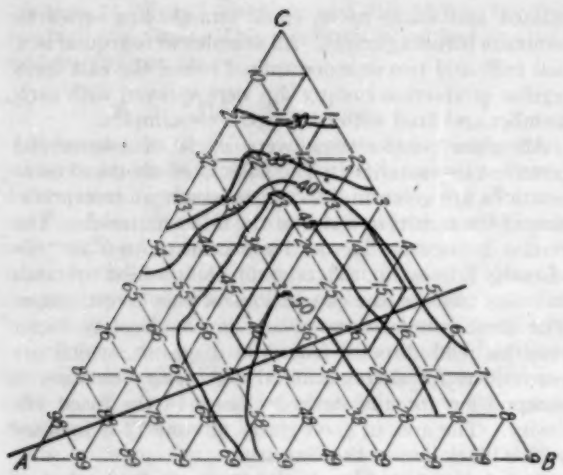

FIG. 3.—Glaze series No. 1 A; composition: feldspar, flint, kaolin, and whiting.

(A)

$$\left.\begin{matrix}CaO\ 0.95\\ K_2O\ 0.03\\ Na_2O\ 0.01\end{matrix}\right\}\ Al_2O_3\ 0.11\quad SiO_2\ 1.06$$

(B)

$$\left.\begin{matrix}CaO\ 0.48\\ K_2O\ 0.40\\ Na_2O\ 0.11\end{matrix}\right\}\ Al_2O_3\ 0.79\quad SiO_2\ 5.59$$

(C)

$$\left.\begin{matrix}CaO\ 0.79\\ K_2O\ 0.16\\ Na_2O\ 0.04\end{matrix}\right\}\ Al_2O_3\ 0.56\quad SiO_2\ 11.79$$

FIG. 4.—Compositions in high silicate section of refractory composition; amount of flow at cone 12.

field in relation to the isoviscosity lines. Critical glazes show marked viscosity changes with small composition changes. All of these studies are based on glazes containing approximately 8 to 10% of kaolin, and these may be used to help in the interpretation of glazes containing slightly more or less kaolin than the amounts listed in the various chemical compositions.

V. Conclusions

(1) Basic Fusion Relations of Feldspar, Flint, Kaolin, and Whiting

The basic series as shown in Fig. 3 is composed of feldspar, flint, kaolin, and whiting and covers that particular portion of the field of glazes between the eutectic composition of these materials, as determined by previous investigators, and the high silica member of the triaxial. The field is sufficiently broad to cover a wide range of commercial compositions and shows the relative effects of high lime and high feldspar glazes.

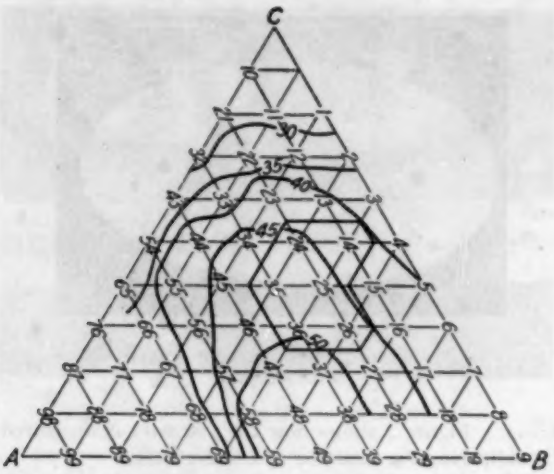

FIG. 5.—Glaze series No. 1 B; composition: feldspar, flint, kaolin, whiting, and tin oxide.

(A)

$$\left.\begin{matrix}CaO\ 0.95\\ K_2O\ 0.03\\ Na_2O\ 0.01\end{matrix}\right\}\ Al_2O_3\ 0.11\left\{\begin{matrix}SiO_2\ 1.06\\ SnO_2\ 0.07\end{matrix}\right.$$

(B)

$$\left.\begin{matrix}CaO\ 0.48\\ K_2O\ 0.40\\ Na_2O\ 0.11\end{matrix}\right\}\ Al_2O_3\ 0.79\left\{\begin{matrix}SiO_2\ 5.58\\ SnO_2\ 0.21\end{matrix}\right.$$

(C)

$$\left.\begin{matrix}CaO\ 0.79\\ K_2O\ 0.16\\ Na_2O\ 0.04\end{matrix}\right\}\ Al_2O_3\ 0.56\left\{\begin{matrix}SiO_2\ 11.84\\ SnO_2\ 0.35\end{matrix}\right.$$

All of the compositions in the high silica section are refractory and have no appreciable flow at cone 12, as may be seen in Fig. 4. Midway between the high feldspar member and the high calcium member is a field of fairly fluid mixtures showing more flow than either the high feldspar or the high calcium member.

The most fluid mixture determined in this investigation contains more calcium than the accepted eutectic value. This is typical of "one-fire" ware and is explained by the partial solution of the body, which has a deficiency in calcium in relation to the glaze composition. In the study of one-fire glazes, the body composition must be taken into consideration.

The isoviscosity lines show the folly of a direct substitution of feldspar for flint to obtain marked changes in fusion characteristics in low calcium compositions. The fused viscosity and brilliancy may be altered more readily by making slight changes in the calcium content.

Of the good glazes made up from the foregoing materials, the most fluid are in the high calcium field and the most viscous are in the high silica field. The sprayed trials show the most fluid mixture (that is, the eutectic taking into consideration body solution) to be overfired at cone 12. The common practice of developing a glaze somewhere between the eutectic composition and the high silica member of the triaxial is an excellent prac-

(*Continued on p. 210*)

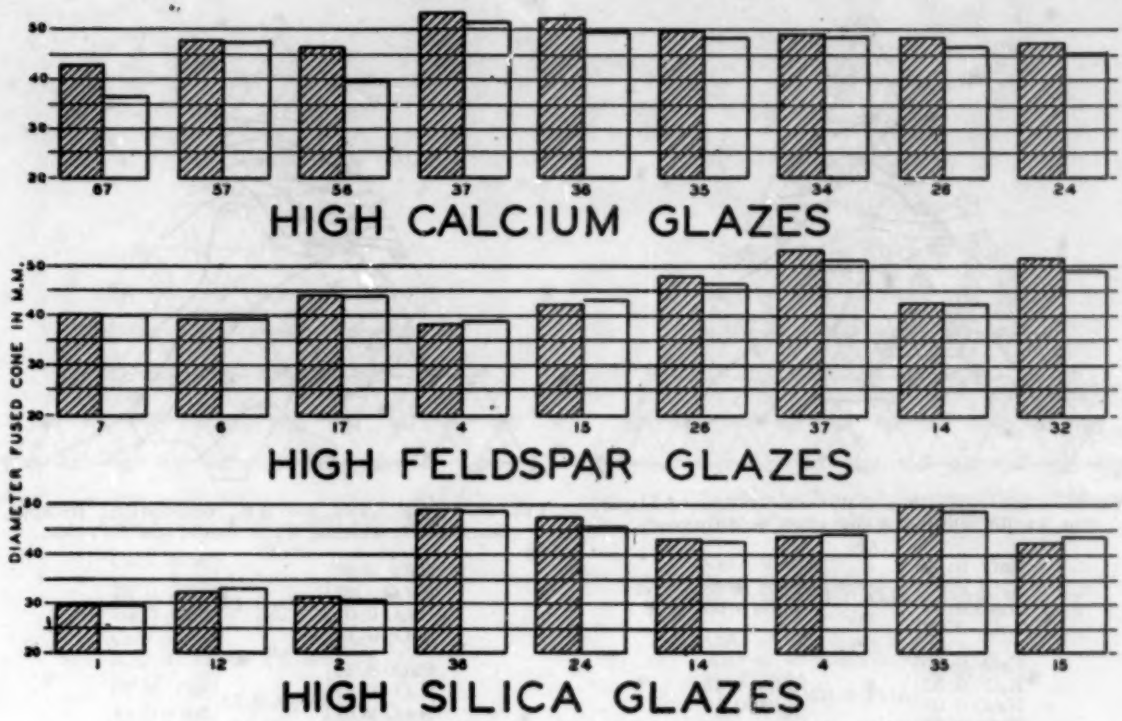

FIG. 6.—Study of tin vs. tinless glazes; open squares, tin glaze; diagonal lines, tinless glaze.

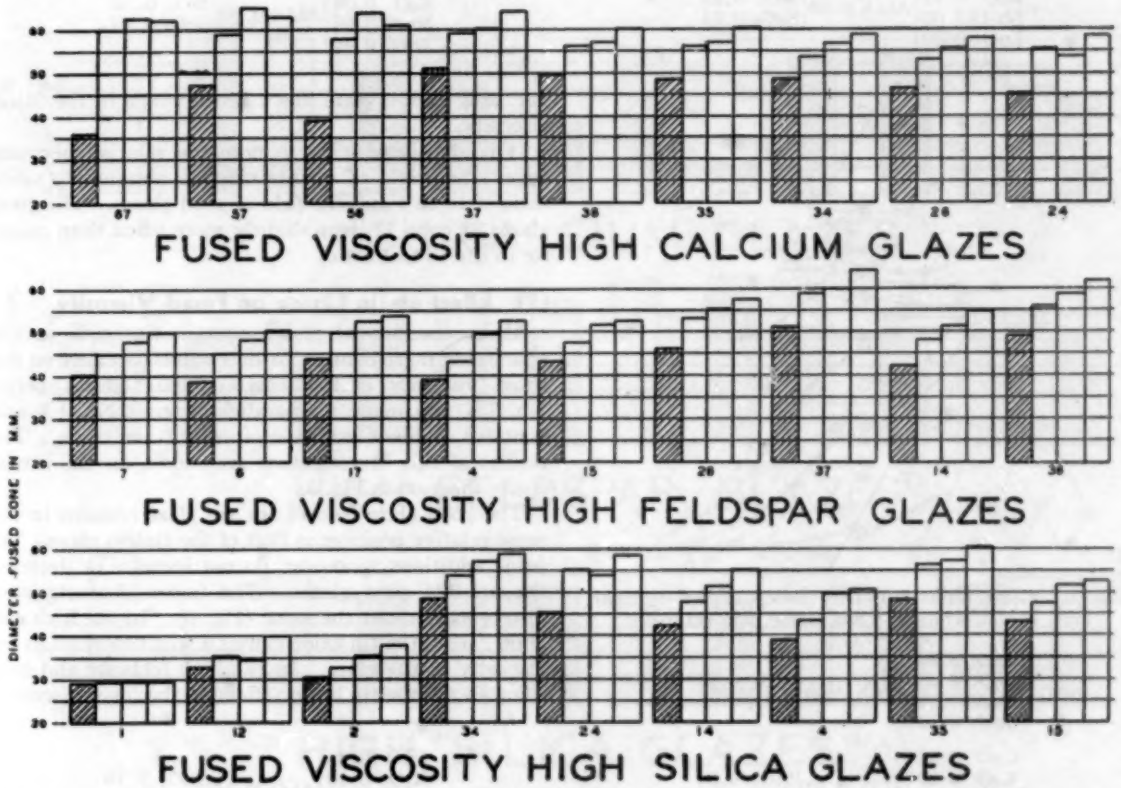
FUSED VISCOSITY HIGH CALCIUM GLAZES
FUSED VISCOSITY HIGH FELDSPAR GLAZES
FUSED VISCOSITY HIGH SILICA GLAZES
DIAMETER FUSED CONE IN M.M.

FIG. 7.—Study of zinc vs. zincless glazes; top, 4%; center, 6%; and bottom, 8%; open squares, zinc glazes; and diagonal lines, zincless glazes.

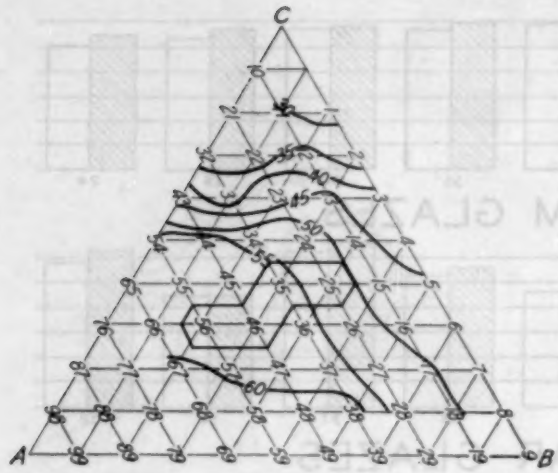

FIG. 8.—Glaze series No. 3 B; composition: feldspar, flint, kaolin, whiting, 4 zinc oxide, and tin oxide.

(*A*)

$$\left.\begin{matrix}CaO\ 0.88\\K_2O\ 0.03\\Na_2O\ 0.01\\ZnO\ 0.08\end{matrix}\right\}Al_2O_3\ 0.10\left\{\begin{matrix}SiO_2\ 0.98\\SnO_2\ 0.06\end{matrix}\right.$$

(*B*)

$$\left.\begin{matrix}CaO\ 0.39\\K_2O\ 0.32\\Na_2O\ 0.08\\ZnO\ 0.20\end{matrix}\right\}Al_2O_3\ 0.63\left\{\begin{matrix}SiO_2\ 4.45\\SnO_2\ 0.16\end{matrix}\right.$$

(*C*)

$$\left.\begin{matrix}CaO\ 0.55\\K_2O\ 0.11\\Na_2O\ 0.03\\ZnO\ 0.30\end{matrix}\right\}Al_2O_3\ 0.39\left\{\begin{matrix}SiO_2\ 8.23\\SnO_2\ 0.24\end{matrix}\right.$$

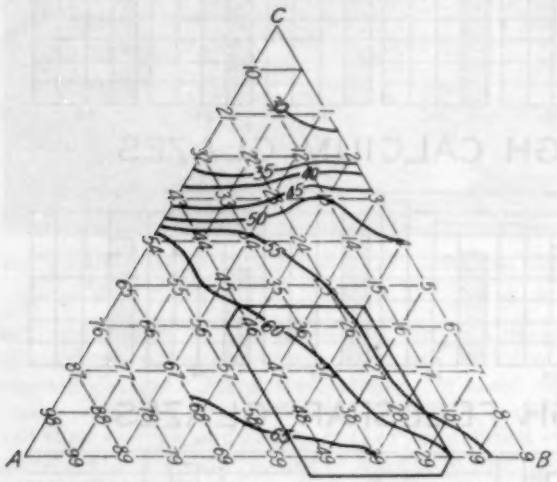

FIG. 9.—Glaze series No. 4 B; composition: feldspar, flint, kaolin, whiting, 6 zinc oxide, and tin oxide.

(*A*)

$$\left.\begin{matrix}CaO\ 0.84\\K_2O\ 0.03\\Na_2O\ 0.01\\ZnO\ 0.12\end{matrix}\right\}Al_2O_3\ 0.10\left\{\begin{matrix}SiO_2\ 0.94\\SnO_2\ 0.06\end{matrix}\right.$$

(*B*)

$$\left.\begin{matrix}CaO\ 0.35\\K_2O\ 0.29\\Na_2O\ 0.08\\ZnO\ 0.28\end{matrix}\right\}Al_2O_3\ 0.57\left\{\begin{matrix}SiO_2\ 4.04\\SnO_2\ 0.15\end{matrix}\right.$$

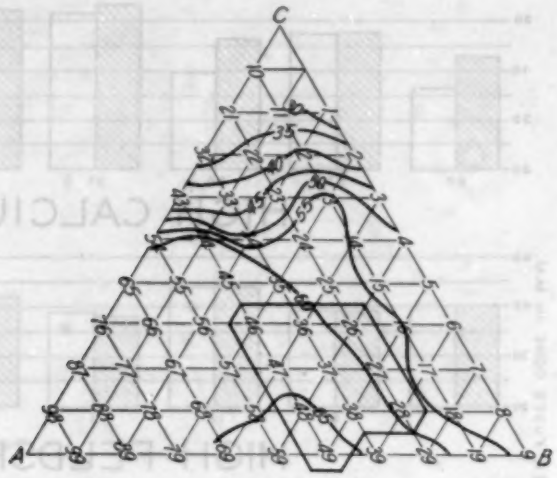

FIG. 10.—Glaze series, No. 5 B; composition: feldspar, flint, kaolin, whiting, 8 zinc oxide, and tin oxide.

(*A*)

$$\left.\begin{matrix}CaO\ 0.81\\K_2O\ 0.03\\Na_2O\ 0.01\\ZnO\ 0.15\end{matrix}\right\}Al_2O_3\ 0.10\left\{\begin{matrix}SiO_2\ 0.91\\SnO_2\ 0.06\end{matrix}\right.$$

(*B*)

$$\left.\begin{matrix}CaO\ 0.32\\K_2O\ 0.27\\Na_2O\ 0.07\\ZnO\ 0.34\end{matrix}\right\}Al_2O_3\ 0.52\left\{\begin{matrix}SiO_2\ 3.70\\SnO_2\ 0.14\end{matrix}\right.$$

(*C*)

$$\left.\begin{matrix}CaO\ 0.42\\K_2O\ 0.08\\Na_2O\ 0.02\\ZnO\ 0.46\end{matrix}\right\}Al_2O_3\ 0.30\left\{\begin{matrix}SiO_2\ 6.33\\SnO_2\ 0.19\end{matrix}\right.$$

tice, and such a glaze has a broad range in the fused viscosity.

It is also interesting to note the relation between Seger's principle of maintaining an alumina to silica ratio of 10 to 1 and the field of good glazes. The good glazes at cone 12 have slightly more silica than called for in the 10 to 1 ratio.

(2) Effect of Tin Oxide on Fused Viscosity

Many commercial glazes contain tin oxide as the opacifying ingredient. To determine its effect on the fused viscosity of the foregoing basic glazes, series No. 1B was made up paralleling series No. 1A and contains a direct addition of 6% of tin oxide. The results of this investigation are shown on the isoviscosity diagram in Fig. 5.

The good glaze field of the tin glaze remains in the same relative position as that of the tinless glaze. Tin oxide additions, moreover, do not increase or decrease the area of good glazes. The fusion characteristics also remain about the same (Fig. 6). In the high calcium glazes, the tin oxide causes a slight increase in the viscosity of the glaze. In the high feldspar and high silica glazes, the tin has no effect on the fused viscosity.

(*C*)

$$\left.\begin{matrix}CaO\ 0.48\\K_2O\ 0.10\\Na_2O\ 0.02\\ZnO\ 0.39\end{matrix}\right\}Al_2O_3\ 0.34\left\{\begin{matrix}SiO_2\ 7.19\\SnO_2\ 0.21\end{matrix}\right.$$

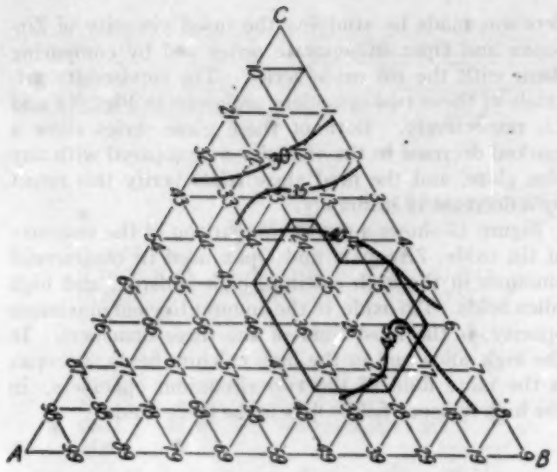

FIG. 11.—Glaze series No. 1 D; composition: feldspar, flint, kaolin, whiting, and Zircopax.

(A)

$$\left.\begin{matrix}CaO\ 0.96\\K_2O\ 0.03\\Na_2O\ 0.01\end{matrix}\right\}Al_2O_3\ 0.11\left\{\begin{matrix}SiO_2\ 1.15\\ZrO_2\ 0.08\end{matrix}\right.$$

(B)

$$\left.\begin{matrix}CaO\ 0.49\\K_2O\ 0.40\\Na_2O\ 0.11\end{matrix}\right\}Al_2O_3\ 0.80\left\{\begin{matrix}SiO_2\ 5.90\\ZrO_2\ 0.25\end{matrix}\right.$$

(C)

$$\left.\begin{matrix}CaO\ 0.80\\K_2O\ 0.16\\Na_2O\ 0.04\end{matrix}\right\}Al_2O_3\ 0.57\left\{\begin{matrix}SiO_2\ 12.44\\ZrO_2\ 0.42\end{matrix}\right.$$

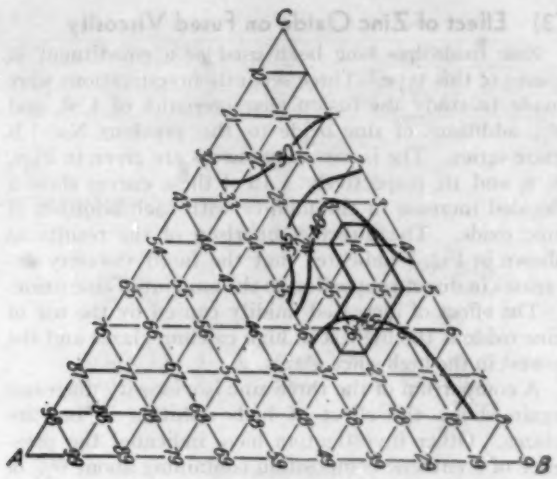

FIG. 12.—Glaze series No. 1 E; composition: feldspar, flint, kaolin, whiting, and Opax.

(A)

$$\left.\begin{matrix}CaO\ 0.96\\K_2O\ 0.03\\Na_2O\ 0.01\end{matrix}\right\}Al_2O_3\ 0.11\left\{\begin{matrix}SiO_2\ 1.08\\ZrO_2\ 0.12\end{matrix}\right.$$

(B)

$$\left.\begin{matrix}CaO\ 0.49\\K_2O\ 0.40\\Na_2O\ 0.11\end{matrix}\right\}Al_2O_3\ 0.80\left\{\begin{matrix}SiO_2\ 5.70\\ZrO_2\ 0.34\end{matrix}\right.$$

(C)

$$\left.\begin{matrix}CaO\ 0.80\\K_2O\ 0.16\\Na_2O\ 0.04\end{matrix}\right\}Al_2O_3\ 0.56\left\{\begin{matrix}SiO_2\ 12.09\\ZrO_2\ 0.58\end{matrix}\right.$$

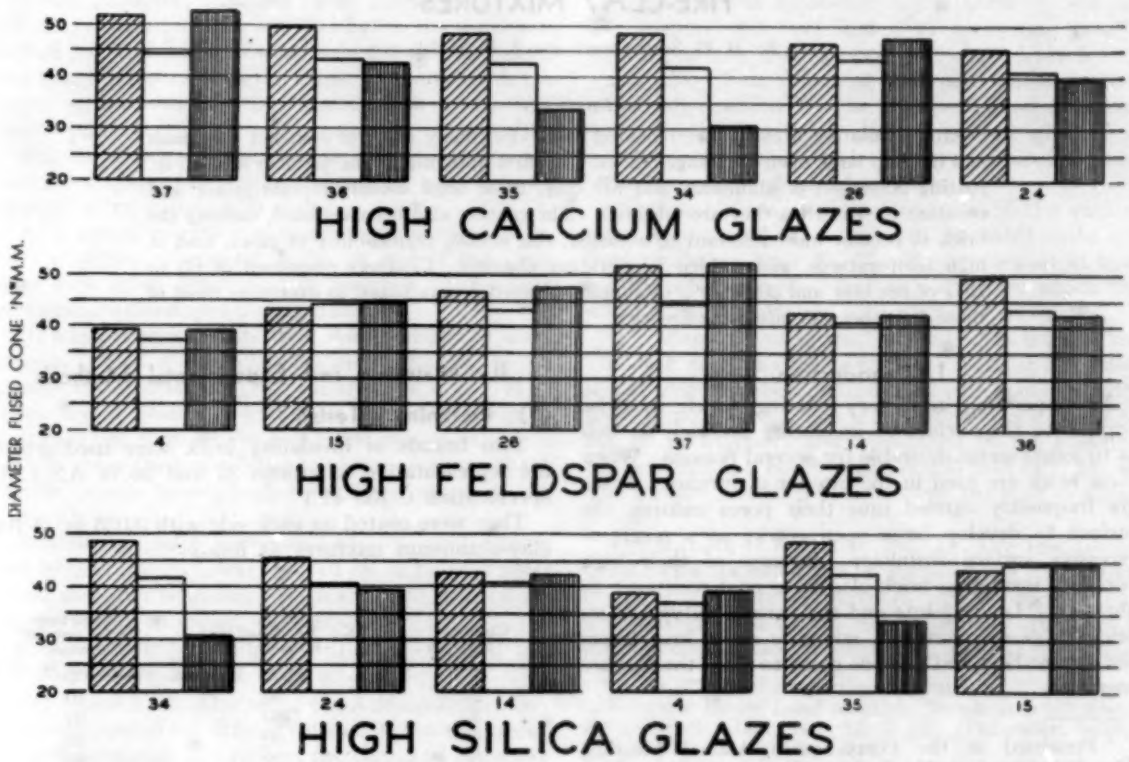

FIG. 13.—Comparison of tin-Zircopax-Opax glazes; open squares, Zircopax; diagonal lines, tin oxide; vertical lines, Opax.

(3) Effect of Zinc Oxide on Fused Viscosity

Zinc oxide has long been used as a constituent in glazes of this type. Three separate investigations were made to study the fusion characteristics of 4, 6, and 8% additions of zinc oxide to the previous No. 1 B glaze series. The isoviscosity curves are given in Figs. 8, 9, and 10, respectively. All of these curves show a decided increase in the fluidity with each addition of zinc oxide. The direct comparison of the results as shown in Fig. 7 indicates that the fused viscosity decreases in direct proportion to the amount of zinc oxide.

The effect of increased fluidity caused by the use of zinc oxide is the highest in high calcium glazes and the lowest in the high silica glazes.

A comparison of the three zinc isoviscosity diagrams again shows the effect of body solution in one-fire glazes. Other investigators have indicated the presence of a eutectic composition containing about 6% of zinc oxide. Because of body solution, the zinc content must be high enough to allow for the feldspar, flint, and kaolin in the body.

(4) Effect of Zircopax and Opax on Fused Viscosity

A direct comparison of tin oxide and zirconium opacifiers was made by studying the fused viscosity of Zircopax and Opax in separate series and by comparing them with the tin oxide series. The isoviscosity triaxials of these two opacifiers are given in Figs. 11 and 12, respectively. Both of these glaze series show a marked decrease in the viscosity as compared with any zinc glaze, and the fired glaze trials verify this result by a decrease in brilliancy.

Figure 13 shows a direct comparison of the viscosity of tin oxide, Zircopax, and Opax used in commercial amounts in the high calcium, high feldspar, and high silica fields. Tin oxide, in the amount to yield maximum opacity, is the most fluid of the three opacifiers. In the high silica and in the high calcium fields, Zircopax is the more fluid of the two zirconium opacifiers; in the high feldspar field, Opax is the more fluid.

Acknowledgment

The writer wishes to express his appreciation to Al Post and to the several laboratory assistants who made up the many test samples for this investigation.

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USE OF ALUMINUM METAL IN THE CERAMIC INDUSTRY: II, EFFECT OF COATING INSULATING FIREBRICK WITH ALUMINUM–FIRE-CLAY MIXTURES*

By H. G. Schurecht and J. F. McMahon

Abstract

After insulating firebrick are reheated in service, many of them contract too much and develop large open shrinkage cracks. By first applying to the surfaces a 0.035-in. coating composed of aluminum and fire clay, these brick usually remain intact and constant in size when they are reheated. The coating also becomes hard, causing the brick to become more resistant to abrasion, slag action, permeability of gases, load at high temperatures, and sudden temperature changes. Coatings composed of 60 to 70% of fire clay and 30 to 40% of aluminum powder were found to overcome most of these deficiencies in insulating firebrick.

I. Introduction

An impervious refractory coating which may be applied to the surface of insulating firebrick as well as to joints seems desirable for several reasons. When these brick are used in the interior of furnaces, fluxes are frequently carried into their pores causing the surface to develop large open cracks as a result of excessive surface shrinkage. Because of their high porosity, insulating brick also have poor resistance to abrasion. Leaky joints and the permeability of these brick to gases, moreover, not only cause heat losses but permit heat and noxious gases to enter the furnace room.

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 21, 1942 (Refractories Division). Received January 25, 1943.

II. Materials and Experimental Methods

(1) Preliminary Tests

Two brands of insulating brick were used which are representative of groups 23 and 26 of A.S.T.M. specification C 155–41 T.

They were coated on each side with 0.035 in. of the clay-aluminum mixtures as follows:

Coating No.	Ky. No. 4 ball clay (−60-mesh) (%)	Aluminum metal powder* (−100-mesh) (%)
1	100	0
2	90	10
3	80	20
4	60	40
5	20	80

* Aluminum powder No. 101 obtained from the Metal Disintegrating Co., Elizabeth, N. J.

TABLE I

Lab. No.	C16	C23	C26	C28	C30	D16	D20	D23	D25	D26	E25
Group No.	16	23	26	28	30	16	20	23	25	26	25
Bulk density (lb./cu. ft.)	20.4	27.9	37.1	38.6	47.3	28.4	30.7	43.1	36.8	41.2	

TABLE II

CHEMICAL ANALYSES AND MOLECULAR FORMULAS OF SLAGS

Multiclone dust

0.0076 Na_2O, 0.0405 K_2O, 0.8826 CaO, 0.0693 MgO | 0.0620 Al_2O_3, 0.0284 Fe_2O_3 | 0.3450 SiO_2, 0.1420 SO_2

	(%)		(%)
SiO_2	20.68	SO_2	11.40
Al_2O_3	6.28	Total K_2O	3.83
Fe_2O_3	4.54	Total Na_2O	0.47
CaO	49.35	Water soluble K_2O	1.77
MgO	2.79		
			101.11

Portland cement clinker

0.9038 CaO, 0.0366 MgO, 0.0596 FeO | 0.0568 Al_2O_3 | 0.3783 SiO_2

	(%)		(%)
SiO_2	21.90	MgO	1.42
Al_2O_3	5.56	SO_3	0.23
Fe_2O_3	4.58	Ignition loss	0.16
CaO	65.30	Free CaO	0.50
			99.60

Soda-lime glass

0.616 Na_2O, 0.384 CaO + MgO | 2.786 SiO_2, 0.0163 B_2O_3

	(%)		(%)
SiO_2	74.4	MgO	8.2
Na_2O	16.9	B_2O_3	0.5
CaO+			
			100.0

Synthetic coal ash

0.027 Na_2O, 0.040 K_2O, 0.226 CaO, 0.301 MgO, 0.406 FeO | 0.306 Al_2O_3 | 1.22 SiO_2

	(%)		(%)
Na_2O	0.99	Al_2O_3	18.64
K_2O	2.27	Fe_2O_3	19.36
CaO	7.56	SiO_2	43.93
MgO	7.25		
			100.00

These refractory coatings were prepared by dry grinding in a ball mill for one hour before the water was added. If the metal powder was allowed to remain too long in contact with the water, it reacted with the water and oxidized with a considerable amount of heat evolution. It was also necessary to keep the aluminum powder in the metallic form to obtain the best results, and the coatings, therefore, were sprayed directly after mixing with water.

After measurements were taken on the sprayed brick, they were fired to cones 6, 8, 10, 13, and 18 and their sizes were again determined to ascertain the amount of shrinkage developed during reheating.

In another series, tests were made on eleven commercial brands of insulating firebrick belonging to the groups 16 to 30 of A.S.T.M. specification C 155–41 T. There are no groups 25 and 30 in the A.S.T.M. specifications, but some of the test brick were classified as such because their properties fall between those of the regular groups having higher and lower numbers (see Table I).

A 0.035-in. coating, composed of 35% of aluminum and 65% of fire clay, was sprayed on all faces of these brick, and after reheating to cones 6, 8, 10, 14, and 18, the amount of shrinkage was measured.

(2) Simulative Service Tests

(*A*) *Load Test:* One set of the A 26 insulating firebrick was coated on all faces with a 0.035-in. mixture of 35% of aluminum and 65% of fire clay, and the other set was left uncoated. The brick were loaded at 9.8 lb. per sq. in., that is, 3.12 lb. per sq. in. for every pound of weight in the brick as recommended by Phelps.[1] The furnace was then heated at a constant rate of 180°C. per hour until the brick deformed $^3/_4$ inch.

(*B*) *Slag Test:* The slag test was similar to that previously described.[2] The slags used were multiclone dust, Portland cement clinker, ground glass, and synthetic coal ash. Table II shows their molecular formulas and the chemical analyses.

Spheres, $^9/_{16}$ in. in diameter, made of the various slags were placed on coated and uncoated slabs cut from insulating brick AC 30 and were heated at temperatures between 800° and 1300°C., after which the relative slag penetration into the body was noted.

(*C*) *Rapid Heating and Cooling and Reheat Test:* This test may be considered a combined spalling and reheat treatment because the brick panels were rapidly heated and cooled. The temperature was brought to 875°C. in 15 hours and was raised to the finishing temperature in 6 hours where it was held for 2 hours. The furnace was then cooled below red heat in about 4 hours.

The furnace is shown in Fig. 1. The test panels in each case consisted of four uncoated and four coated brick, which were set without mortar joints. The heat was supplied with a Maxon premix burner which entered the furnace through the bottom; the flame

[1] S. M. Phelps, "Properties of Insulating Refractories: I, Behavior Under Load at High Temperatures," *Amer. Refrac. Tech. Bull.*, No. 61, 6 pp. (December, 1935); *Ceram. Abs.*, **15** [7] 209 (1935).

[2] H. G. Schurecht, "Reaction of Slag with Refractories: I, Surface Reactions of Slags with Refractories," *Jour. Amer. Ceram. Soc.*, **22** [4] 116–23 (1939).

was directed against a silicon carbide slab which spread the heat uniformly to the sides of the furnace.

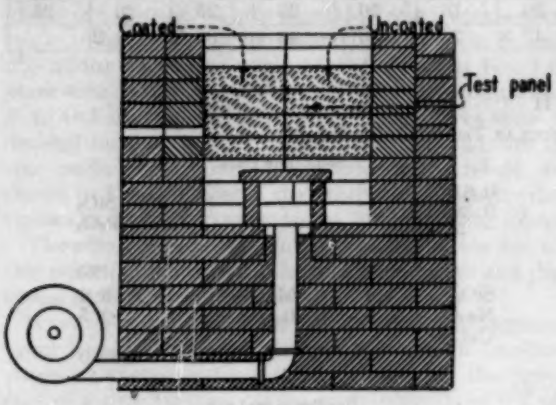

FIG. 1.—Furnace used for simulative spalling and reheat tests.

The panels were heated successively to 1230°, 1310°, 1400°, 1450°, and 1500°C. After each cycle, the brick were removed to measure shrinkage and to examine them for cracks and other defects.

III. Results

The influence of coatings composed of varying aluminum–fire-clay contents on the reheat shrinkage of two brands of insulating firebrick are given in Table III, and the appearance of the B brick after reheating to cone 18 are shown in Fig. 2. The fired coatings were hard and impervious and therefore apparently also increased the resistance of the brick to abrasion and permeability to gases.

Table IV gives the test results on the influence of a coating composed of 35% of aluminum powder and 65% of fire clay on the reheat shrinkage of eleven brands of insulating brick.

The temperatures at which the coated and uncoated

TABLE III

INFLUENCE OF DIFFERENT ALUMINUM–FIRE-CLAY COATINGS ON SHRINKAGE OF INSULATING FIREBRICK AFTER REHEATING

	Coating (composition %)		Volume and linear shrinkage (−) or expansion (+) after reheating (%)*									
			Cone 6		Cone 8		Cone 10		Cone 13		Cone 18	
No.	Ball clay	Aluminum metal powder	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
A1	0	0	0	0	0	0	0	0	0	0	−13.0	−4.5
A2	100	0	0	0	0	0	3.4	1.1	−0.25†	−0.8	− 8.8†	−3.0
A3	90	10	0	0	0	0	2.8	0.9	0.9	0.3	− 7.3	−2.5
A4	80	20	0.3	0.1	−0.2	−0.07	2.6	0.9	0.2	0.07	− 5.3	−1.8
A5	60	40	0	0	−1.77	−0.6	0.84	0.28			− 2.2	−0.7
A6	20	80	0‡	0‡	0‡	0‡	0.4‡	0.1‡	0.4‡	0.1‡	3.0‡	1.0‡
B1	0	0	0	0	1.59	0.5	2.32	0.8	−1.0	−0.3	−20.0	−7.2
B2	100	0	0	0	−2.00	−0.7	0	0	−4.8†	−1.6	−21.2†	−7.6
B3	90	10	0	0	−0.30	−0.1	1.23	0.40	−2.8	−0.9	−14.9	−5.2
B4	80	20	0	0	0.15	0.08	0.57	0.18	−0.25	−0.8	− 6.1	−2.1
B5	60	40	−0.21	−0.07	0.92	0.30	1.00	0.30	1.02	0.3	2.5	0.8
B6	20	80	0‡	0	0.12‡	0.03	1.10‡	0.37	0.50‡	0.17	7.8‡	2.5

* Columns (1), volume shrinkage; columns (2) linear shrinkage.
† Vitreous coating. ‡ Small cracks developed in coating which extended into body.

TABLE IV

INFLUENCE OF 35% ALUMINUM 65% FIRE-CLAY COATING ON SHRINKAGE OF INSULATING FIREBRICK IN REHEAT TESTS

		Volume and linear shrinkage (−) or expansion (+) after reheating (%)*									
		Cone 6		Cone 8		Cone 10		Cone 13		Cone 18	
No.	Treatment	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
C16	Coated	2.1	0.7	2.1	0.7	2.1	0.7	4.0	1.3	−21.7†	− 7.8
	Uncoated	0	0	− 0.5	− 0.17	− 0.5	− 0.17	−19.3	− 6.9	−48.8†	−20.0
C23	Coated	0	0	0	0	0	0	− 4.2	− 1.4	−61.3†	−27.1
	Uncoated	0	0	0	0	0	0	− 3.7	− 0.9	−68.8†	−32.2
C26	Coated	0	0	0	0	0	0	0	0	0	0
	Uncoated	0	0	0	0	0	0	0	0	− 4.7	− 1.6
C28	Coated	0	0	0	0	− 0.5	− 0.17	0	0	− 0.9	− 0.3
	Uncoated	0	0	0	0	0	0	0	0	− 2.1	− 0.7
C30	Coated	0	0	0	0	− 2.1	− 0.7	0	0	− 2.1	− 0.7
	Uncoated	0	0	0	0	− 2.1	− 0.7	0	0	− 2.1	− 0.7
D16	Coated	−22.1	− 7.97	−22.0	− 8.00	−26.9	− 9.9	‡			
	Uncoated	−42.2	−16.70	−43.0	−17.10	−48.8	−20.0	‡			
D20	Coated	− 6.1	− 2.08	− 2.40	− 7.1	− 9.0	− 3.1	−18.5	− 6.6	−31.1†	−11.7
	Uncoated	− 8.2	− 2.80	−12.1	− 4.2	−15.9	− 5.6	−29.8	−11.1	−55.4†	−23.6
D23	Coated	0	0	0	0	− 2.1	− 0.7	− 8.1	− 2.8	−14.0	− 4.9
	Uncoated	0	0	0	0	− 3.6	− 1.2	− 6.2	− 2.1	−20.3	− 7.3
D25	Coated	0	0	0	0	0	0	− 5.3	− 1.8	−17.7†	− 6.3
	Uncoated	0	0	0	0	0	0	− 4.1	− 1.4	−22.9†	− 8.3
D26	Coated	0	0	0	0	0	0	0	0	−11.4§	− 3.8
	Uncoated	0	0	0	0	0	0	− 2.7	− 0.9	−24.4	− 8.9

* Columns (1), volume shrinkage (%); columns (2) linear shrinkage (%).
† Badly distorted. ‡ Melted. § Slightly distorted.

FIG. 2.—Effect of aluminum–fire-clay coatings on shrinkage of group of twenty-six insulating firebrick reheated to cone 18; sample No. 1, original brick as received; No. 2, uncoated brick (note shrinkage); No. 3, coated with 100% of ball clay; No. 4, coated with 90% of ball clay and 10% of aluminum; No. 5, coated with 80% of ball clay and 20% of aluminum; No. 6, coated with 60% of ball clay and 40% of aluminum (note expansion by referring to black line); No. 7 coated with 20% of ball clay and 80% of aluminum (note expansion).

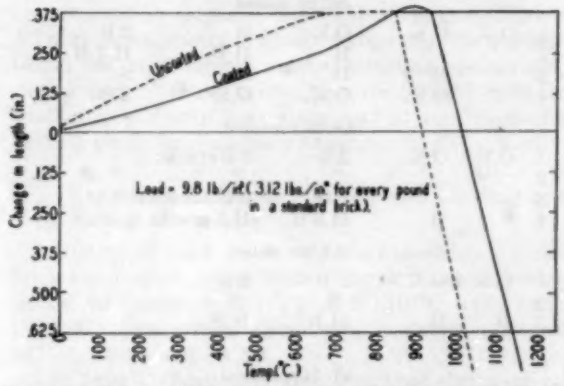

FIG. 3.—Change in length of coated and uncoated brick during load test.

brick started to deform in the load test and at which they settled ¾ in. are as follows:

	Temp. of initial deformation (°C.)	Temp. at which brick deformed ¾ in. (°C.)
Uncoated	862	1038
Coated	938	1165

The deformation measurements made throughout the tests have been plotted in Fig. 3, and Fig. 4 shows the influence of the coatings on the resistance of brick to slag action.

The results of the rapid heating and cooling tests on panels are given in Tables V and VI, and the appearance of some of these panels after the tests is shown in Fig. 5.

IV. Discussion of Results

(1) Preliminary Tests

When the brick were sprayed with coatings composed of varying amounts of aluminum and fire clay, little shrinkage took place until they were reheated to cone 10 or higher (see Table III).

When fired to cone 18, brick A with no coating developed a linear shrinkage of 4.5%; a 100% ball-clay coating reduced this to 3.0%; and the 10% aluminum and 90% ball-clay coating lowered it to 2.5%. The

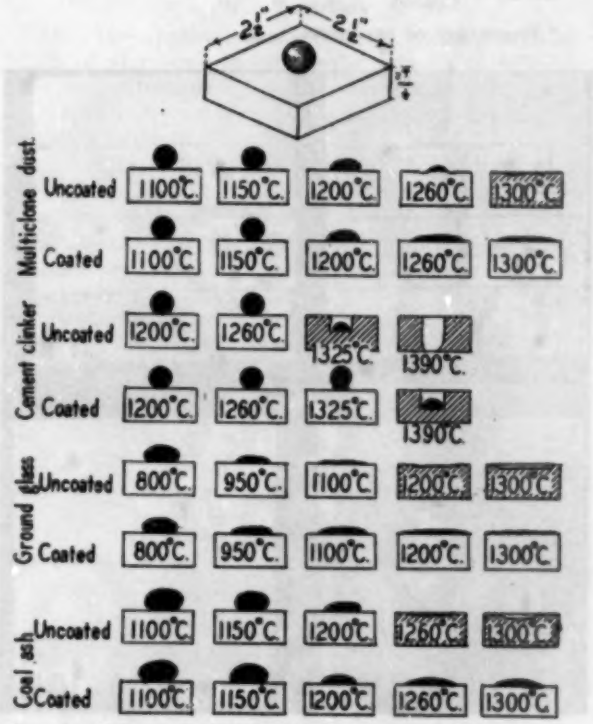

FIG. 4.—Effect of aluminum coatings on resistance of lightweight refractories to slag action.

brick coated with 60% of ball clay and 40% of aluminum shrank about 0.7%; and a 20% ball-clay and 80% aluminum-powder coating caused it to expand 1%.

Shrinkage of firebrick at high temperatures is probably the result of cohesive forces which tend to cause the brick to occupy as small a volume as possible. Because the shrinkage forces cannot be greater than the strength of the pyroplastic fire clay at furnace temperatures, they must be small, especially at high temperatures. When metallic aluminum metal is oxidized into aluminum oxide, it expands about 32% in volume, and coatings containing high percentages

TABLE V

SHRINKAGES OF EXPOSED FACES IN THE REHEAT TESTS

Brand	Treatment	Linear shrinkage of brick (%) 1230° C.	1310° C.	1400°C.	1450°C.	1500°C.
		Along 9-in. length of exposed face				
AC 30	Uncoated	0	0	0.7	0.7	0.7
	Coated	0	0	0	0	0
AC 26	Uncoated	0	0	0	0	0.7
	Coated	0	0	0	0	0
AE 25	Uncoated			0.7	1.4	
	Coated	0	0	0.7*	1.4*	
AD 25	Uncoated	0	0	1.4		
	Coated	0	0	0		
		Along 2½-in. width of exposed face				
AC 30	Uncoated	0	0	2.5	2.5	2.5
	Coated	0	0	0	0	0
AC 26	Uncoated	0	0	2.5	2.5	3.7
	Coated	0	0	0	0	0
AE 25	Uncoated	0	0	3.7	5.0	
	Coated	0	0	0	0	
AD 25	Uncoated	0	0	3.7		
	Coated	0	0	0		

* Percentage of expansion.

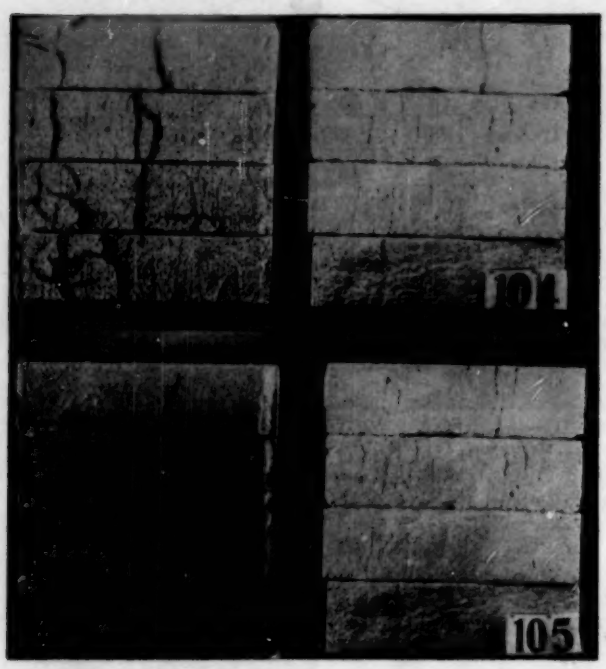

FIG. 5.—Influence of coating of 35% of alumina and 65% of fire clay on cracking of insulating firebrick; sample No. 104, AD 25 brick panels after heat-treatment at 1400°C., *left*, uncoated and *right*, coated; sample No. 105, AE 25 brick panels after heat-treatment at 1450°C., *left*, uncoated, and *right*, coated.

of aluminum therefore have a tendency to expand on being heated. This force evidently is sufficient to counteract shrinkage forces of the fire clay, and where the coating contained a high content of aluminum, it actually caused the brick, which was pyroplastic at high temperatures, to expand.

Similar results were obtained with brick B (see Table I and Fig. 2).

TABLE VI

APPEARANCE OF BRICK AFTER HEATING ON ONE FACE IN SIMULATIVE SPALLING AND REHEAT TESTS*

Brick No.	Heating temp. (°C.) 1230	1310	1400	1450	1500
			AC 30 uncoated		
1	Crack	Crack	Crack	Crack	S crack
2	O.K.	O.K.	O.K.	O.K.	2 B
3	"	"	"	"	O.K.
4	"	H	H	H B	H B
			AC 30 coated		
1	H	H	H	H B	S
2	"	"	"	"	H B
3	"	"	"	H	"
4	"	"	"	"	"
			AC 26 uncoated		
1	O.K.	O.K.	O.K.	O.K.	S crack
2	"	"	"	"	3 B 2 cracks
3	"	"	"	B	3 B crack
4	"	"	"	"	B 2 cracks
			AC 26 coated		
1	O.K.	O.K.	O.K.	B	2 B
2	"	"	H	H B	H 3 B
3	"	H	H	H	S
4	"	O.K.	O.K.	O.K.	2 B
			AE 25 uncoated		
1	O.K.	O.K.	2 B	2 B cracks	
2	"	"	"	" "	
3	"	"	2 C	2 C 3 cracks	
4	"	H	H 2 B	H 3 cracks	
			AE 25 coated		
1	O.K.	O.K.	2 B	2 B	
2	"	"	"	"	
3	H	H	H B	H B	
4	"	"	"	"	
			AD 25 uncoated		
1	O.K.	2 cracks	2 cracks		
2	"	" "	3 "		
3	"	" "	6 "		
4	"	" "	4 "		
			AD 25 coated		
1	O.K.	O.K.	2 B		
2	B	B	"		
3	O.K.	O.K.	"		
4	H	H	H 2 B		

* H, hair crack on exposed side; crack, open shrinkage cracks on exposed side; B, crack on 9- by 4½-in. side; S, broken in two.

(2) Effect of 35% Aluminum Coating on Different Brick

When the eleven different brands of insulating firebrick were sprayed with a coating composed of 35% of aluminum and 65% of clay, the reheat shrinkage was reduced in many cases (see Table IV). Although this coating lowered the shrinkage, it did not entirely prevent it in brick belonging to groups 16 to 25 except in one brick fired to cone 18. It is probable, however, that the brick which developed only slight shrinkage at high temperatures would not have shrunk at all if the aluminum content had been raised to 40 or 45% in the coating.

This aluminum-clay coating, however, entirely prevented shrinkage in some of the insulating firebrick

in group 26 to 30. Group 16 to 23 brick shrank much less when coated with aluminum-clay mixtures than when they were uncoated, but the coating does not prevent shrinkage of brick made of low refractory clays when heated to cone 18. It is evidently possible to raise low number groups to higher number groups by coating them with suitable aluminum–fire-clay mixtures.

(3) Load Test

It is apparent from Fig. 3 that the aluminum coating has slightly increased the resistance of the brick to deformation at high temperatures, and the coating is beneficial insofar as the brick load-carrying capacity at high temperatures is concerned even though this coating is only 0.032 in. thick.

(4) Slag Resistance

Figure 4 shows that the uncoated insulating firebrick are attacked by slags much more than the coated brick. All of these slags were of a basic nature, but the coatings would not have offered much protection against acid slag action.[3] These brick, however, would come in contact chiefly with basic slags, and in most cases this coating would increase their resistance to slag action.

(5) Resistance to Rapid Heating and Cooling and to Reheat Shrinkage

In the panel tests, where only the exposed side of the brick was coated, group 26 to 30 brick developed practically no shrinkage at 1230° and 1310°C. (see Table IV). Hairline cracks developed, however, on brick AC 30, AE 25 and AC 26.

The 1400°C. heating produced marked shrinkage on the exposed face of all of the uncoated brick. The percentage of shrinkage along the $2^1/_2$-in. width was much greater than it was along the 9-in. length. Small hairline cracks developed on the 9- by $4^1/_2$-in. face near the coating on brick AE 25 and AD 25, but these cracks were not serious.

The more serious cracks, $^1/_8$ to $^1/_4$ in. wide, developed on the exposed face of the uncoated brick, AD 25 and AE 25 (see Fig. 5). The exposed faces of the coated brick developed small hairline cracks in two cases, whereas fine checking occurred on the 9- by $4^1/_2$-in. face near the coating. The AC 26 and AC 30 brick developed fine hairline cracks on both coated and uncoated brick at this temperature, but these cracks were not serious.

After firing to 1500°C., the uncoated AC 26 brick showed surface shrinkage cracks, and the coated brick were only slightly checked. The AC 30 uncoated brick also shrank more than the coated brick.

V. Summary

(1) The application of a 0.035-in. coating of 35 to 45% of aluminum metal powder and 55 to 65% of fire clay to insulating brick lowered the shrinkage and in many cases prevented it entirely on reheating to cone 18.

(2) This coating also increased the resistance of insulating firebrick to reheat shrinkage, cracking on the exposed faces, load at high temperatures, basic slag action, abrasion, permeability to gases, and rapid heating and cooling.

Acknowledgment

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[3] H. G. Schurecht, "Reactions of Slag with Refractories: II, Refractory Coatings Produced with Metallic Aluminum," *Jour. Amer. Ceram. Soc.*, **22** [11] 384–88 (1939).

STUDY OF LITERATURE ON SEPARATION OF MAGNESIA FROM LIME IN DOLOMITE AND SIMILAR MATERIALS*

COMPILED BY GILBERT E. SEIL† AND STAFF‡

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I. Introduction

There is an increasing need for improved processes of recovering magnesia from dolomite, magnesite, magnesium-bearing salt brines, and similar raw materials. A literature survey of methods dating from 1817 to 1943 has been made of the physical and chemical processes and combinations of these processes for extracting magnesia from these raw materials. No attempt has been made to evaluate the processes either economically or otherwise.

The older methods are concerned chiefly with physical means of extraction such as pulverizing, classifying, leaching, and flotation, whereas the more recent methods resort to chemical separation.

II. Physical Extraction

Although practically all methods of separation classified as chemical resort also to physical means, the following processes depend chiefly on such physical characteristics as size of particle, temperature of calcination, degree of hydration, solubility, and susceptibility to flotation reagents.

(1) Classifying

Auzies and Segoffin (19, 21)§ prepare pure magnesia by calcining dolomite and placing it in a tank transversed by a stream of water. This tank is connected with a series of other tanks in steps so that the stream of water flows from tank to tank. The lighter MgO is carried to the farthest tank, and the CaO is retained in the first tanks by reason of its greater weight. Mellor (65) employs the same method. Mitchell (76) heats ground dolomite to 540° while it is being tumbled, and it is ground again to decompose the dolomite to MgO and $CaCO_3$. The MgO is then separated by classifying with water. According to Kilbourn (132, 143), materials containing both $CaCO_3$ and $MgCO_3$ are calcined, slaked, and allowed to settle. They are then subjected to the action of a stream of water introduced beneath a 200-mesh screen covered with a layer of porous material so that the lime is floated off and the magnesia remains. McLaughlin (62) claims that relatively pure MgO can be made from magnesite containing silica by calcining to drive off the CO_2, quenching the hot calcined product to affect its disintegration, and sieving out the coarse silica. The material is ground to pass a 30-mesh screen and subjected to currents of air or water so adjusted as to carry away material of specific gravity of 2.2 and leave material of specific gravity of 3 or more.

(2) Calcination

One of the physical methods of obtaining magnesia from dolomite is by the selective calcination of the dolomite. Considerable data have been collected relating to the calcination of dolomite and magnesite (36, 52, 116, 141, 157, 159, 165, 168, 180, 181, 192, 229, 298, 337, 374, 423, 428). Garnett (131, 167) claims that dolomite does not dissociate in distinct stages as a mixture of the two carbonates. Potapenko (246), however, shows that the decomposition of the $MgCO_3$ in dolomite starts after heating for one hour in CO_2 at 725° but $CaCO_3$ does not start to decompose until 850°. A Russian article (286) states that the decomposition of the $MgCO_3$ at 760° to 800° is complete in one hour whereas the decomposition of the $CaCO_3$ occurring under these conditions is insignificant. Perederil (327) claims that the dissociation of $MgCO_3$ takes place between 390° and 660° and that the dissociation of $CaCO_3$ does not begin until 720°. An Austrian patent (135) states that $MgCO_3$ is decomposed at 500° to 600° whereas the $CaCO_3$ is left unchanged. In order to make sure that the calcined dolomite contains no free lime, MacIntire (365) subjects dolomite of 100-mesh fineness to a current of steam at 500° to 550°. Any free lime formed is thus dissolved out as soluble $Ca(OH)_2$.

Shaw and Bole (136) obtain the separation of magnesia and lime by heating the dolomite in a closed chamber so that at any temperature the CO_2 pressure

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§ For references in parentheses, see Bibliography, pp. 228–36.

inside the chamber is lower than the dissociation pressure of $MgCO_3$ but higher than the dissociation pressure of $CaCO_3$ at that temperature. Only the $MgCO_3$ is decomposed in this way, giving a mixture of MgO and $CaCO_3$ which can be separated mechanically. A French patent (348) states that when the partial pressure of CO_2 is 40% the temperature of the reaction should be within the range 650° to 750° but when the partial pressure is 80% the temperature may be raised to 800°.

Fréchette (66) heats a mottled pink and white high lime magnesite to about 1000° in the electric furnace; some of the product formed is pink and some is white. The pink part analyzes MgO 96.90% and CaO 1.85%, and the white part gives MgO 44.42% and CaO 54.82%. On treating the calcined material with water, the white part slakes and can be removed from the gritty pink part leaving a pure magnesia.

A U. S. patent (250) heats dolomite in an ordinary lime kiln operating at a temperature somewhat lower than usual. This affects the decomposition of substantially all of the $MgCO_3$ to MgO without decomposing the $CaCO_3$, except to a limited extent. The inner cone of $CaCO_3$ and MgO is separated from the outer cone of CaO and MgO by the action of a water spray.

According to a German patent (174), impure magnesite or rock containing magnesite is burned at temperatures at which the secondary minerals are so little affected that their hardness remains practically unchanged. The material is granulated, and the secondary minerals are removed by sieving.

Booth (331, 372) calcines dolomite by bringing it into contact with a molten inorganic compound, such as NaCl or KCl, which is substantially inert to both constituents. The temperature is kept above the decomposition point of $MgCO_3$ and below the decomposition point of $CaCO_3$, making sure the molten compound is stable at that temperature.

A U. S. patent (400) reduces $MgSO_4$ to MgO by passing a mixture of $MgSO_4$ and coal into a furnace heated to about 900°. The reducing agent is in such proportions as to effect full reduction of not more than about 50 to 70% of the $MgSO_4$ to MgO. The reduction is then completed at temperatures up to 1000° in contact with a gaseous reducing agent.

(3) Hydration

Goudge (385, 427) suggests recovering magnesia from brucitic dolomite or brucite rock by calcining the rock and then hydrating the calcine under carefully controlled conditions with just sufficient water to convert the lime into hydroxide while leaving granules of MgO. The MgO is then removed by an air separator. Kiepenheuer (51) gives data on the degree of hydration of calcined dolomite.

(4) Leaching

The difference in the solubility of MgO and CaO in water has been used to obtain substantially lime-free magnesia from dolomite (75, 98, 106, 383). The dolomite is calcined, and the lime is leached out by means of a large quantity of water. A British patent (363) suggests using 500 liters of water per kilogram of solid, making sure the water is free from bicarbonates, CO_2, or added chemicals. Duschak (99) obtains almost complete leaching of the lime by burning the dolomite at 900° to 950°, but he states that if the dolomite is dead-burned the extraction is incomplete and is not improved by fine grinding, probably because of the formation of an insoluble compound. Sisson (20) leaches calcined dolomite with sea water, thereby increasing the yield obtained from the soluble magnesium salts in solution which are converted to additional MgO by the lime in the dolomite. Chesny (401) removes soluble impurities from $Mg(OH)_2$ by supporting the $Mg(OH)_2$ on a moving conveyer in a layer 2.5 cm. thick while a solvent at 25° to 50° flows along the conveyer in a direction opposite to the movement of the $Mg(OH)_2$.

(5) Flotation

Many methods of concentrating magnesite and dolomite ores by means of flotation have been suggested (384, 390, 391, 394, 410, 426). DuBois (251) first calcines the dolomite to $CaCO_3$ and MgO and then projects the finely ground product into an emulsion of water and oil or hydrocarbon. The $CaCO_3$ is retained in the foam, and the MgO passes into the liquor. In a two-stage, froth-flotation method of beneficiating a magnesium ore, siliceous gangue is floated off by means of methyl amyl alcohol in the first stage whereas the magnesium ore is floated from a further amount of gangue in the second stage, according to a patent by Fahrenwald (421).

(6) Crystallization

One of the purely physical means of producing pure magnesium salts is to crystallize them from brines, sea water, and other solutions containing them (38, 59, 205, 227, 230, 237, 243, 311, 312, 379). The crystallization of the magnesia is accomplished only after other soluble salts have been removed by previous crystallization. In all of the processes, temperature must be closely controlled at all stages of the crystallization. Barstow (57) adds $Mg(OH)_2$ and then SO_2 to brine in order to convert the $CaCl_2$ into insoluble $CaSO_3$. This $CaSO_3$ is filtered off, and the $MgCl_2$ is recovered from the solution by evaporation after the removal of the NaCl. Meshcheryakov (397) states that preliminary evaporation and precipitation of other salts before separating $MgCl_2$ are not economically practical.

Instead of crystallizing out the pure magnesium salts, Heath (235) precipitates tachydrite, $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$, by concentrating the solution under reduced pressure. Collings (218, 231) dissolves these tachydrite crystals in a limited quantity of water and then crystallizes $MgCl_2 \cdot 6H_2O$ from the solution. The filtrate retains the $CaCl_2$ in solution.

Two Japanese investigators (369, 370) obtain $MgCl_2$ by a different method. Bittern is concentrated by heating above 100° to precipitate $K_2SO_4 \cdot 2MgSO_4$. The mother liquor is then cooled and $KCl \cdot MgCl_2 \cdot 6H_2O$ precipitates out. The two solids are combined and dissolved in water. Double decomposition takes place, yielding crystalline $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ and

leaving aqueous $MgCl_2$ as the mother liquor from which pure $MgCl_2$ can be recovered.

Crystallization can also be used to recover magnesia from ores after the ore has been dissolved by some solvent. Schoch (217) treats an ore, such as polyhalite, with hot water to obtain a solution of K_2SO_4 and $MgSO_4$. The K_2SO_4 is separated from the solution by crystallization, and the $MgSO_4$ is recovered. A Russian patent (342) proposes to dissolve minerals containing boron and magnesium with H_2SO_4, crystallize H_3BO_3 from the solution, and then precipitate the $MgSO_4$ by heating and concentrating the mother liquor. The remaining liquor is returned to the extraction process.

Jackson, in a U. S. patent (85), dissolves siliceous magnesium ores with alkali and water under heat and pressure. The insoluble material is filtered off and dissolved in acid to bring the magnesium and heavy metals into solution. The solution is digested with Na_2CO_3 to precipitate any iron which may be present, and the magnesium salt is then separated by crystallization.

(7) Miscellaneous Physical Methods

Many physical methods of recovering magnesia from dolomite and other magnesium-bearing raw materials have been reviewed (107, 351, 352, 373, 380, 396). These give procedures for the application of physical methods of extraction and compare methods according to cost, purity of product, and time consumed. Krotov (175) and Bruet (378) give geological data on the origin of dolomite, limestone, and magnesite.

III. Chemical Extraction

Although the cost of chemical separation of magnesium compounds from impurities with which they occur in the natural state is greater than that required by the foregoing physical processes, the products obtained are purer. Impurities, such as iron, alumina, and lime, may be removed by intricate and accurately controlled measures, which accounts for the comparatively high cost of magnesium and its compounds.

The following chemical methods are grouped according to the principal reagent used in the extraction.

(1) Forming Carbonates and Formates

(*A*) *Carbon Dioxide:* A method which has been employed extensively for the production of lime-free MgO uses CO_2 to react on slaked calcined dolomite to produce insoluble $CaCO_3$ and soluble $Mg(HCO_3)_2$, which solution, if boiled, precipitates $MgCO_3$ (4, 22, 31, 40, 110, 140, 142, 151, 220, 283, 367).

Greider (252) adds a crystallization retarding agent, such as gelatin, gum arabic, sulfonated castor oil, or an alkali metal compound of casein or saponin, before heating the bicarbonate solution in order to precipitate a light $MgCO_3$. An English firm (422) recovers the magnesia from the bicarbonate by adding to the solution $Mg(OH)_2$, which is prepared from sea water and dolomite and which precipitates basic magnesium carbonate. A French patent (202) suggests the use of calcined MgO to precipitate the basic carbonate. Obukhov (303) electrolyzes the bicarbonate, obtaining $Mg(OH)_2$, which is calcined to MgO.

Tagnon (223) and DuBois (236) calcine dolomite at a temperature, which decomposes the $MgCO_3$ but not the $CaCO_3$, and then proceed with the slaking and carbonation. According to a German patent (15), powdered charcoal, paraffin, or another hydrocarbon oil is used as a repressing agent for CO_2, which keeps the mass in a loose porous condition. Shelyagin (268) employs 1 to 2% of a sulfonic acid of the benzene, naphthalene, or quinoline series, such as petroleum sulfonic acid or alizarin oil, as a catalyst for the carbonation.

Two methods (125, 128) carbonate the calcined dolomite in the presence of gypsum. A solution containing the mixed salts of $MgSO_4$ and $Mg(HCO_3)_2$ is thus obtained. If this solution is boiled, $MgCO_3$ precipitates and can be filtered off leaving the pure $MgSO_4$ in solution, from which solid $MgSO_4$ can be crystallized by evaporation. Moritz (193, 196) carries out the carbonation in the presence of $MgCl_2$.

Platzmann, in a series of articles (197, 264, 325), suggests adding $KHCO_3$ before passing in the CO_2. Insoluble $CaCO_3$ precipitates leaving a carbonate of the general formula $MgCO_3 \cdot KHCO_3 \cdot H_2O$ in solution. This is filtered off and heated to 100° whereby $MgCO_3 \cdot 3H_2O$ precipitates out. This carbonate is filtered off and calcined to magnesia.

Instead of carbonating at normal pressures, the efficiency of the conversion can be increased by treating slaked calcined dolomite with CO_2 at a pressure of 5 to 6 atmospheres at a temperature slightly above normal (2, 3, 5, 11, 26, 28, 58, 118, 124, 154, 163, 225, 241, 244, 280). A similar process (41, 114, 147, 155) treats slaked, calcined dolomite with a solution of an alkali carbonate or bicarbonate and CO_2 under pressure at 60° to 70°. The liquor containing $KHCO_3 \cdot MgCO_3 \cdot H_2O$ is filtered and heated to 100°, whereby $MgCO_3$ precipitates and leaves alkali carbonate solution for re-use in the process. A French firm (187, 190) adds any potassium salt to $MgCO_3$ and subjects the mixture to CO_2 under pressure. Kiepenheuer (164) precipitates $MgCO_3$ from the mixed carbonate solution simply by reducing the pressure of CO_2. Hambloch (139) recovers the magnesium as $MgCO_3 \cdot 3H_2O$ by heating the mixed carbonates in vacuum. A German firm (144, 153) adds MgO or $Mg(OH)_2$ to the carbonate solution to recover the $MgCO_3$.

Stump (404) claims that calcium may be separated from magnesium in an aqueous suspension of $Ca(OH)_2$ and MgO by passing CO_2 continuously into the suspension and maintaining equimolar concentrations of $Ca(OH)_2$ and $CaCO_3$. The calcium becomes carbonated, and the magnesium remains in stable suspension. Both are continuously removed from the precipitating vessel. Black (113) slakes dolomite with water saturated with lime and then treats the slaked mass with CO_2 in an amount not quite sufficient to precipitate all of the $Ca(OH)_2$. The MgO, which has been unaffected by this treatment, is recovered from the suspension. Pike (112) states that the soluble lime content of calcined MgO is reduced by agitating

the material in a closed vessel at a temperature of 300° to 600° in the presence of a gas containing CO_2 and a trace of water vapor.

According to a U. S. patent (238), dolomite is burned at a temperature at which only the $MgCO_3$ is decomposed, and the product is ground and treated with sufficient water to hydrate the MgO. The mass is then treated with CO_2 to form $MgCO_3$ and is heated until dry to form a basic magnesium carbonate. This basic carbonate is then separated from $CaCO_3$ by air separation and heated in order to decompose it into MgO.

Laird (296) slakes calcined dolomite and adds HCl to the slurry in an amount equal to the $Mg(OH)_2$ present. This mixture is then subjected to CO_2 to precipitate $CaCO_3$ and leave $MgCl_2$ in solution. MacMullin (304) treats a mixture of $CaCl_2$ and $MgCl_2$ with free oxygen and water vapor at 400° to 700°. The resulting mixture of MgO and $CaCl_2$ is then carbonated to precipitate $CaCO_3$ from the solution of $MgCl_2$.

Galt (69) recovers the magnesium content of sludge resulting from causticizing Na_2CO_3 with hydrated calcined dolomite by treating it with water and CO_2 under pressure. The $Mg(HCO_3)_2$ solution is filtered, heated to precipitate $MgCO_3$, and the $MgCO_3$ is then digested with a solution of $CaCl_2$ to produce $MgCl_2$.

Brandenburg (387) calcines serpentine at 500° to 900°, liberating MgO, and he then suspends the calcine in water while passing CO_2 through the solution. Soluble $Mg(HCO_3)_2$ is formed, which is filtered and converted to MgO by heating the solution and then calcining the precipitated $MgCO_3$.

(*B*) *Carbonates:* Hambloch and Gelleri (34, 35) prepare pure $MgCO_3$ by igniting dolomite with a magnesium silicate, with or without the addition of lime or limestone. The reaction proceeds according to equation (1).

$$3MgO \cdot 4SiO_2 \cdot H_2O + 4CaCO_3 \rightarrow 3MgO + 4CaO \cdot SiO_2 \quad (1)$$

The product of the reaction is treated at normal temperature and pressure with $(NH_4)_2CO_3$ solution. The MgO is dissolved out as $MgCO_3 \cdot (NH_4)_2CO_3$, and the $CaO \cdot SiO_2$ remains as a residue. The double salt obtained is converted into $MgCO_3$ by heating, according to reaction (2).

$$MgCO_3 \cdot (NH_4)_2CO_3 \rightarrow MgCO_3 + 2NH_3 + CO_2 + H_2O \quad (2)$$

The liberated NH_3 and CO_2 are collected to form $(NH_4)_2CO_3$ for re-use in the process.

Moritz (184) uses calcined dolomite to causticize a Na_2CO_3 solution, thereby forming soluble $Mg(HCO_3)_2$ and insoluble $CaCO_3$. The two are separated and pure $MgCO_3$ is prepared from the $Mg(HCO_3)_2$ by heating.

A Russian article (357) suggests dissolving serpentine in H_2SO_4, HNO_3, or HCl and then neutralizing this solution with more serpentine. The solution is filtered and carefully treated with Na_2CO_3 to precipitate iron and nickel, and then more Na_2CO_3 is used to precipitate basic $MgCO_3$. The precipitation is carried out best from a manganese-free concentrated solution at high temperature.

In order to obtain $MgCO_3$ from bitterns containing magnesium salts, such as $MgSO_4$ and $MgCl_2$, Grunwald (82) adds a mixture of Na_2CO_3 and $NaHCO_3$ to liberate CO_2, which precipitates the magnesia as $MgCO_3$. Schoch (270) treats polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, with an amount of $CaCO_3$ equivalent to the $MgSO_4$ present and then heats the wetted mixture to above 150° in a closed vessel, producing $Mg(OH)_2$.

Barstow and his associates (277) use $MgCO_3$ to prepare pure $MgCl_2$ from a mixture of $CaCl_2$ and $MgCl_2$. The mixed chlorides are treated with $MgCO_3$ yielding insoluble $CaCO_3$ and $MgCl_2$ which contain a small amount of $CaCl_2$. These are separated by filtration. The $MgCl_2$ is further purified by suspending $Mg(OH)_2$ in the $MgCl_2$ solution and passing CO_2 through the solution, which completely removes the $CaCl_2$ as $CaCO_3$ and leaves pure $MgCl_2$ as a product.

(*C*) *Carbon Monoxide:* If calcined and slaked dolomite is treated with CO under pressure, soluble calcium formate is formed, leaving MgO (271, 274, 275). The calcium formate is leached out and may be converted to formic acid, alkali formate, or K_2CO_3. A French patent (333) describes the treatment of $MgSO_4$ with CO at about 750°, yielding MgO, SO_2, and CO_2.

(2) Chlorine Compounds

(*A*) *Chlorine:* Magnesium is separated from calcium in dolomite by calcining and then treating the calcine with chlorine in such amounts that only $CaCl_2$ is formed. This is filtered from the MgO, which is left in a pure state (185, 186, 301, 307). Sano (313) gives physical chemical data for the reaction.

(*B*) *Hydrochloric Acid:* Magnesia can be extracted from olivine by reacting it with HCl to form $MgCl_2$ and H_2SiO_3 (425). If water is kept at a minimum by using concentrated HCl, a large part of the water in the system will be taken up by the hydration of $MgCl_2$, leaving the H_2SiO_3 in a granular condition. If excess water is present, however, a gel forms which coats the olivine, absorbs acid and $MgCl_2$ and generally interferes with the reaction. Treatment with concentrated HCl followed by leaching removes virtually all of the $MgCl_2$.

In a British patent (68), dolomite is converted to $CaCl_2$ and MgO by the use of HCl gas produced by the reaction of steam on $AsCl_3$. The MgO and $CaCl_2$ are then separated by lixiviation. According to a patent assigned to the Dow Chemical Company (201), raw dolomite is dissolved in HCl. This solution is then treated with hydrated calcined dolomite, and the precipitated $Mg(OH)_2$ is separated by filtration from the solution of $CaCl_2$. A French process (226) dissolves raw dolomite in HCl and then adds slaked calcined dolomite while passing CO_2 through the solution. In this case, the $MgCl_2$ stays in solution and leaves a residue of $CaCO_3$.

A concentrated solution of $MgCl_2$ can be obtained from any magnesiferous compound by the use of HCl gas (323, 389, 416). The HCl in the gaseous state is passed in the presence of steam through lumps of the material to be decomposed. The temperature is kept between 100° and 500° under normal pressure. The steam and the $MgCl_2$ condense in the cooler part of the system yielding a concentrated solution of $MgCl_2$.

(*C*) *Calcium Chloride:* A solution of $CaCl_2$ may be employed in several ways to recover MgO from dolomite. If the dolomite is calcined first and mixed with $CaCl_2$ alone, soluble calcium hyprochlorite and insoluble $Mg(OH)_2$ are formed (25, 27, 91, 101, 123) according to equation (3).

$$MgO \cdot CaO + CaCl_2 + H_2O \rightarrow Ca_2OCl_2 + Mg(OH)_2 \quad (3)$$

The $Mg(OH)_2$ is filtered off and calcined to produce MgO. Carbon dioxide from the calcining kilns is then passed into the filtrate precipitating $CaCO_3$ and producing a solution of $CaCl_2$ for re-use in the process.

If, instead of reacting the $CaCl_2$ solution with calcined dolomite, it is reacted with uncalcined dolomite or the mixed carbonates of magnesium and lime, soluble $MgCl_2$ is formed as well as insoluble $CaCO_3$ (61, 96). The soluble $MgCl_2$ can be converted to $MgCO_3$ with CO_2.

Galt (70) describes the production of $MgCl_2$ by heating the $CaCl_2$ liquor from the ammonia-soda process with the sludge resulting from causticizing Na_2CO_3 with hydrated calcined magnesia.

Another method of utilizing $CaCl_2$ is to calcine dolomite until the $MgCO_3$ is completely converted to MgO, mix this material with $CaCl_2$, and then subject the mixture to CO_2 either under normal pressure (14, 29, 100, 104, 108, 172, 177, 189, 203, 305, 306, 314, 316, 346) or under increased pressure (228, 318). Soluble $MgCl_2$ and insoluble $CaCO_3$ are formed and are separated by filtration. An Austrian patent (295) claims that the filtration proceeds more easily if boric acid or an alkali borate is added.

Robinson (95) produces $CaCO_3$ and MgO from dolomite by calcining the dolomite, mixing it with a solution of $CaCl_2$ in such proportions that the MgO is chemically equivalent to the $CaCl_2$ and, when the mixture is thoroughly slaked and mixed passing CO_2 through it to convert all the lime to $CaCO_3$. The $MgCl_2$ formed is filtered from the $CaCO_3$ and agitated with dolomite in such proportions that the lime in the dolomite is chemically equivalent to the MgO in the solution. The solution is boiled and filtered, and the $Mg(OH)_2$ is calcined.

$MgCl_2$ and $CaCO_3$ are made (54) by passing a solution of $CaCl_2$ containing $Mg(OH)_2$ in suspension downward through a reaction tower filled with nonporous inert material while passing combustion gases or other gases containing less than 30% of CO_2 upward through the tower. The use of dilute CO_2 prevents the formation of $Mg(HCO_3)_2$ and $MgCO_3$.

Peacock (64) employs $CaCl_2$ for the preparation of $MgCl_2$ from silicate rocks containing magnesium, such as talc or serpentine. The silicates are comminuted and digested with more than 10% excess of $CaCl_2$ in aqueous solution at a boiling temperature or under a pressure of 80 to 90 pounds per square inch. This pressure renders the reaction more rapid and complete. The $MgCl_2$ is recovered by dissolving it out of the reaction mixture.

(*D*) *Magnesium Chloride:* The simplest method of utilizing $MgCl_2$ to prepare pure magnesia is to mix calcined and slaked dolomite with $MgCl_2$ solution, in which case $Mg(OH)_2$ precipitates out, leaving $CaCl_2$ in solution (14, 43, 48, 95, 100, 104, 108, 203, 302, 314, 319, 346, 349, 405). A German patent (50) uses a similar process but prepares the $MgCl_2$ from $MgSO_4$ lye and the $CaCl_2$ obtained in the process.

Another process mixes raw dolomite and $MgCl_2$ and calcines the mixture (138, 176, 177). The $CaCl_2$ formed is dissolved leaving magnesia. A similar method mixes raw dolomite and $MgCl_2$ and then calcines them in the presence of CO_2 under ordinary pressure (316). Schulze (340, 347) conducts the process at 150° and at the CO_2 pressure necessary to maintain the liquor at that temperature. A French patent (297) uses a emperature between 170° and 200° in an autoclave n a mixture of the calcined dolomite and $MgCl_2$.

A German firm (44) and Clerc and Nihoul (148), in similar processes, employ $MgCl_2$ for the final purification of their magnesia. The dolomite is completely calcined and then treated with a calculated amount of water not quite sufficient to slake the lime content of the dolomite. Under these conditions, the MgO is not slaked. The slaked lime is now specifically lighter than the MgO and can be separated from it by physical means. Because the MgO still contains some lime that was not slaked, it is mixed with a $MgCl_2$ lye, which converts the CaO to $CaCl_2$ and yields nearly pure MgO.

Because the $Mg(OH)_2$ precipitated in the above reactions is hard to filter, many methods have been proposed to make the filtration easier. One process adds the $MgCl_2$ in the presence of ammonia or ammonium salts (305, 306). Lee (388) calcines the dolomite with a small amount of material providing a member of the group that consists of beryllium and boron and then mixes this calcined material with the $MgCl_2$ solution.

Another method of obtaining an easily filtered $Mg(OH)_2$ is to react slaked dolomite with $MgCl_2$ at raised temperature in a medium in which has been dissolved large amounts of substances such as alkali or alkali-earth nitrates or chlorides, particularly $CaCl_2$ (292, 338). Wienert (371) slakes calcined dolomite with an aqueous solution containing an alkali metal or alkali-earth metal nitrate, alkali metal chlorate, or $CaCl_2$, together with a small amount of boric acid or alkali borate, and then adds the $MgCl_2$ solution.

Chesny (393, 413) employs a special process for the production of $Mg(OH)_2$ from dolomite and $MgCl_2$. The dolomite is calcined to convert substantially all the carbonate to oxide. A slurry is made of the calcined dolomite that is mixed in a vessel to which an aqueous solution containing convertible magnesium salts is admitted so as to impart to the body of the liquid a gentle rotary or swirling motion. The slurry is introduced below the surface of the aqueous solution so as to prevent or minimize the production of hydrous $Mg(OH)_2$. The liquid is thereafter passed with its precipitate to another vessel for the separation of the precipitated hydroxide.

(*E*) *Cyclic:* The cyclic processes involving $CaCl_2$ and $MgCl_2$ are all similar. One type (14, 95, 100, 104, 108, 177, 203, 314) treats calcined dolomite with $MgCl_2$ producing soluble $CaCl_2$ and pure MgO. These are separated by filtration, and the $CaCl_2$ is then re-

acted with calcined dolomite in the presence of CO_2 obtained from the calcination in order to produce insoluble $CaCO_3$ and soluble $MgCl_2$, which are separated by filtration. The $MgCl_2$ is returned to the circuit, and the $CaCO_3$ is rejected.

Dougherty (308) conducts his cycle similarly but uses H_2SO_4 instead of CO_2 with the $CaCl_2$ solution to produce insoluble $CaSO_4$ rather than $CaCO_3$. The $MgCl_2$ resulting at the same time is used to produce $CaCl_2$ and $Mg(OH)_2$ by reaction with a mixture of the hydroxides.

A process patented by a German firm (305, 306) is similar to the first cyclic method mentioned except that ammonia or ammonium chloride is added to the process and is continually recovered and recirculated in the process with the $CaCl_2$ and $MgCl_2$.

Another process (316) uses CO_2 with both the $MgCl_2$ and $CaCl_2$ treatments. The advantage of this process is that $MgCO_3$ may be obtained directly without carbonation.

A different cyclic process, which seems to be less economical, is one patented by Perani (346). The first series of reactions form a mixture of MgO and $CaCl_2$ from $MgCl_2$ and dolomite as in the first cyclic process mentioned. Only part of this MgO is filtered off as the final product; the remainder is combined with the $CaCl_2$ in the presence of CO_2 to produce $MgCl_2$ for re-use in the process.

A patent assigned to Dow Chemical Company (343) describes the preparation of pure $MgCl_2$ and pure $CaCl_2$ from a mixture of the salts using dolomite. The process consists of reacting dolomite with a brine containing $MgCl_2$ and $CaCl_2$ to produce $CaCO_3$ and an impure $MgCl_2$ solution containing some $CaCl_2$. The $CaCO_3$ is calcined and slaked and the $Ca(OH)_2$ produced is added to a portion of the original brine, producing a pure $CaCl_2$ solution and precipitating $Mg(OH)_2$. This $Mg(OH)_2$ is added to the impure $MgCl_2$ from the first step in the presence of CO_2, producing pure $MgCl_2$ and precipitating a mixture of calcium and magnesium carbonates. These carbonates are added with additional dolomite to the first step of the process. The $MgCl_2$ and $CaCl_2$ obtained by this method are pure and free from contamination by each other.

According to a patent applied for by the Harbison-Walker Refractories Company (430), calcined dolomite is hydrated with $CaCl_2$ solution instead of water. This produces a granular hydrate, probably because of the formation of calcium oxychloride cement. The hydrates are seasoned for twelve hours, then milled and air-separated into coarse granules and fines. The fines are suspended in $CaCl_2$ solution and treated with CO_2, producing $MgCl_2$ and insoluble $CaCO_3$. The $MgCl_2$ solution is filtered off and added to the coarse granules which have been made into a slurry with $CaCl_2$ solution. This $Mg(OH)_2$ which is produced is filtered off and leaves $CaCl_2$ solution, which is used to react with the fines.

A completely different type of cyclic process is one assigned to the Dow Chemical Company (200). Fused $MgCl_2$ is electrolyzed to obtain magnesium and free chlorine. The free chlorine is converted into HCl, which is made to react with dolomite, giving a mixture of $MgCl_2$ and $CaCl_2$. These chlorides are separated, and the $MgCl_2$ is used to replenish the bath.

(*F*) *Manufacture of Hydrochloric Acid:* In the manufacture of HCl from $MgCl_2$ (16, 30, 32, 37, 39, 102, 247), pure MgO is obtained as a by-product after washing the residue free from chlorides. The original $MgCl_2$ in solution is mixed with magnesia or magnesium carbonate to form magnesium oxychloride. The oxychloride is dried and completely dehydrated and is then subjected to a stream of superheated steam and air. A Russian method (282) uses a CO_2 steam mixture. HCl and MgO are formed according to equation (4).

$$Mg_3OCl_2 + H_2O \rightarrow 2HCl + 2MgO \qquad (4)$$

If the $MgCl_2$ contains $CaCl_2$, the latter is unchanged in the process and can be removed from the MgO by washing. Optimum temperature for the reaction is between 450° and 700° (18, 109, 208, 248). To facilitate the decomposition of the oxychloride, Beck (89) adds 2 to 5% of $MgSO_4$ to the mixture before drying.

In treating dolomites, Dutt (88) dissolves the material in HCl, removes the iron and other impurities by use of an alkaline earth oxide or hydroxide, filters them off, evaporates the filtrate to dryness, and proceeds as in the other methods.

Tocco (171) uses hydrogen instead of steam for the production of HCl. In this case, the hydride instead of the oxide is formed. A temperature above 700° is necessary for the decomposition of $MgCl_2$ with hydrogen.

(3) Nitric Acid

When calcined dolomite is treated with HNO_3, the CaO is converted to $Ca(NO_3)_2$ whereas the MgO is unaffected (266). Cambi (210) starts with a dolomite containing 20.78% of MgO and 31.2% of CaO and recovers a final product containing 98.91% of MgO and 0.39% of CaO. He shows by two definite breaks in the electrometric titration that $Ca(NO_3)_2$ forms first after which $Mg(NO_3)_2$ forms.

A different method (221, 232, 233, 255) dissolves dolomite in HNO_3 and then adds to the solution more dolomite, which has been calcined and slaked. The lime content of both additions of dolomite goes into solution precipitating $Mg(OH)_2$. Twynam (179) states that the precipitated hydroxide may be separated by physical means from the heavier MgO of the burnt dolomite. In a series of patents (261, 267, 276, 278), Klöckner-Werke uses this same principle but makes the precipitation in the presence of ammonia or an ammonium salt.

The magnesium content of serpentine and olivine may be recovered by treating them with HNO_3 of 25 to 40% strength at 50° to 90° in order to convert the magnesium to a soluble nitrate, leaving the silicic acid in an easily filterable state (111, 121, 122).

(4) Sulfur Compounds

(*A*) *Sulfuric Acid:* The purpose of treating dolomite with H_2SO_4 is to convert the lime to insoluble $CaSO_4$ and the magnesia to soluble $MgSO_4$ (209, 260, 279, 320). The products are separated by filtration,

and the $MgSO_4$ can then be converted by Na_2CO_3 to $MgCO_3$, which in turn can be calcined to MgO (219). Two U. S. patents (150, 308) propose calcining the dolomite and adding $CaCl_2$ before adding the H_2SO_4 in order to obtain $MgCl_2$ instead of $MgSO_4$. Dougherty (315) adds free chlorine to the calcined dolomite before precipitating the $CaSO_4$.

Laurent and Baze (234), instead of using H_2SO_4, pass SO_2 gas into a pulp containing finely ground dolomite. The same result is obtained.

Sulfuric acid can also be used to obtain pure $MgCl_2$ from $MgCl_2$ solutions containing a small amount of $CaCl_2$, according to Barstow (83). A series of German patents (45, 47, 63) utilizes waste $MgCl_2$ lye from the potash industry by mixing this lye with H_2SO_4 and distilling over the HCl produced. The $MgSO_4$ remaining in the solution is crystallized out by evaporation.

Peacock (55) recovers the magnesium content of serpentine and other magnesium-bearing minerals by treating them with somewhat less H_2SO_4 than would be required to combine with all the magnesium present. The heat of reaction is allowed to rise high enough to prevent formation of gelatinous silica. The $MgSO_4$ formed is recovered by lixiviation and crystallization.

A Norwegian process (117) decomposes olivine or serpentine with 30 to 60% of H_2SO_4 at a temperature which is gradually increased from 60° to 104°. The materials are so finely ground that the main reaction takes place between 80° and 90°.

(*B*) *Sodium Sulfate:* Sodium sulfate is added to a solution of mixed magnesium and calcium salts, precipitating $CaSO_4$ and leaving soluble $MgSO_4$. These are separated by filtration, and the $MgSO_4$ solution is treated with Na_2CO_3 to precipitate $MgCO_3$, which may then be calcined to pure magnesia. Pozdeev (285) treats a brine solution directly. Dolomite can be dissolved in HCl and then treated in this manner (87, 213). According to a Canadian patent (78), Elliott treats magnesite containing SiO_2 and CaO with an acid leach containing chlorine to dissolve the magnesite. The SiO_2 is removed by filtration, and the lime is precipitated by the addition of a soluble sulfate.

(*C*) *Sodium Bisulfate:* If $NaHSO_4$ is added to dolomite, which has been calcined and slaked, insoluble $CaSO_4$ is precipitated, leaving $MgSO_4$ in solution (12, 161, 272). Magnesia can be prepared from the solution by converting it to $MgCO_3$ and then calcining. Barstow (84) uses $NaHSO_4$ to react on a mixture of calcium and magnesium chlorides in a similar manner.

(*D*) *Calcium Sulfate:* If hydrated calcined dolomite is treated with gypsum in the presence of CO_2, soluble $MgSO_4$ is formed leaving a precipitate of $CaCO_3$ (127, 129, 145, 269). A patent assigned to the Morton Salt Company (402) does not use CO_2 but mixes the dolomite and gypsum in the presence of 1 to 2% of free $Mg(OH)_2$, based on the weight of $MgCO_3$ present in the suspension. This percentage of $Mg(OH)_2$ is maintained until a 70% conversion is reached.

(*E*) *Magnesium Sulfate:* Magnesium sulfate is used to convert the lime of calcined dolomite to gypsum, which may then be separated from the magnesia hydrate by centrifuging (9, 199). Instead of centrifuging, another method (67) treats the $MgSO_4$ mixture under pressure with CO_2-containing gases in the presence of excess water to give a solution of $Mg(HCO_3)_2$ from which the $CaSO_4$ formed is removed.

(*F*) *Sulfur Dioxide:* If finely divided dolomite is suspended in water and then subjected to the action of sulfur dioxide and air, soluble $MgSO_4$ is formed leaving the insoluble $CaCO_3$ (94, 120). Stump (253) partially calcines dolomite to a mixture of MgO and $CaCO_3$ and then subjects it to this treatment. Barstow (97) adds $CaCl_2$ to slaked calcined dolomite and passes a mixture of CO_2 and SO_2 gas into the suspension to produce soluble $MgCl_2$. A Japanese patent (256) uses a mixture of SO_2 and Cl_2 on powdered raw dolomite A German patent (53) utilizes the waste $MgCl_2$ lye from the potash industry by subjecting it to a mixture of SO_2 and air in the presence of steam.

(*G*) *Sulfites:* Barstow (56) adds to brine containing $MgCl_2$, $CaCl_2$, and NaCl a quantity of $MgSO_3$ equivalent to the $CaCl_2$ content. Insoluble $CaSO_3$ precipitates out leaving $MgCl_2$ and NaCl in solution. These may then be separated by crystallization. The $MgSO_3$ is prepared by adding $Ca(OH)_2$ to another portion of the brine and treating the $Mg(OH)_2$ precipitated with SO_2. Another patent (92) suggests removing the lime content of brine by the addition of Na_2SO_3 or a mixture of Na_2SO_3 and Na_2CO_3.

Drewsen (162) boils slaked calcined dolomite with the waste magnesium monosulfite liquor produced in the digestion of fibrous vegetable material, precipitating $Mg(OH)_2$. This $Mg(OH)_2$ is further purified by dissolving it in excess CO_2 to form $Mg(HCO_3)_2$, which is filtered from these impurities.

(*H*) *Sulfur, Sulfides, Hydrogen Sulfide:* Drewsen (170) treats slaked dolomite with sulfur to produce CaS and $Mg(OH)_2$, which are then separated. A British patent (79) heats a mixture of dolomite and CaS to dull redness in a stream of air, water vapor, and CO_2. Soluble $MgSO_4$ is separated from the residue of $CaCO_3$ by lixiviation. Brandenburg (395) calcines a mixture of serpentine and pyrites producing $MgSO_4$, which is dissolved in water and filtered off. The solution can then be concentrated to $MgSO_4 \cdot 7H_2O$ of a purity of about 99.75% and free from iron.

Hydrogen sulfide can be utilized in the production of lime-free magnesia in two ways. One method (119, 336) calcines dolomite at a temperature which will decompose only the $MgCO_3$ and not the $CaCO_3$. The semicalcined mass is slaked and H_2S is injected into the slurry. Soluble $Mg(HS)_2$ forms and is filtered from the $CaCO_3$, which is unaffected. Boiling the solution of $Mg(HS)_2$ produces $Mg(OH)_2$ and regenerates the H_2S. The Warner Company (431) calcines dolomite completely, slakes the mixture, and then adds H_2S in an amount equivalent to the CaO present. The calcium goes into solution as $Ca(HS)_2$ leaving the $Mg(OH)_2$ as a residue, which is filtered and calcined to MgO. The H_2S is recovered and pure $CaCO_3$ is produced by carbonating the $Ca(HS)_2$ solution.

5) Ammonia and Ammonium Salts

According to a series of patents assigned to Klöckner-Werke (290, 293, 344), dolomite is dissolved in HNO_3, and $Mg(OH)_2$ is precipitated by the addition of NH_3. The $Mg(OH)_2$ may then be calcined to MgO. Monterumici (126) treats calcined dolomite with an ammonium salt such as the sulfate or chloride and then adds NH_3 to precipitate a part of the $Mg(OH)_2$. The precipitate is separated by filtration, and the mother liquor is used to treat more crude material. A Russian process (294) adds to the dolomite an amount of NH_4NO_3 equivalent to the lime content and then treats the mixture with liquid NH_3 at 20° to 40°. The $Ca(NO_3)_2$ formed is separated from the residue, and to the residue is added an amount of NH_4NO_3 molecularly equivalent to the MgO content. This mixture is further treated with liquid NH_3 at −40° to form $Mg(NO_3)_2$ solution, which is separated from the insoluble material and freed from NH_3 by heating. Urbain (215) introduces calcined dolomite into an ammoniacal solution in the presence of CO_2, producing $Mg(CO_3)_2 \cdot (NH_4)_2CO_3$.

In a number of patents (173, 183, 191, 207, 211, 212, 222, 224, 245), NH_4Cl is used for the extraction of magnesia from dolomite. The calcined dolomite is treated with a solution of NH_4Cl, producing a solution of $CaCl_2$ and a residue of $Mg(OH)_2$ which can be separated by filtration. Two other patents (23, 204) suggest regenerating the NH_4Cl solution by recovering the NH_3 produced in the process and passing the gas through the $CaCl_2$ solution in the presence of CO_2. $CaCO_3$ is precipitated leaving NH_4Cl. Barrett (249) recovers the NH_4Cl by adding $(NH_4)_2CO_3$ to the solution of $CaCl_2$.

Windecker (258) treats calcined dolomite with NH_4Cl liquor in slightly more than the quantity theoretically required to convert all the lime to $CaCl_2$. This solution is filtered off, and the residue is then treated with additional NH_4Cl to convert the MgO to $MgCl_2$, leaving the impurities undissolved. The $MgCl_2$ may then be filtered off as a substantially pure solution.

Bradburn (49) mixes slaked calcined dolomite with NaCl and NH_4Cl until the calcium and magnesium are both dissolved and then removes the NH_3 formed by distillation. The remaining liquor is treated with fresh calcined dolomite, which effects precipitation of $Mg(OH)_2$ and separation of MgO from the dolomite. The $Mg(OH)_2$ and MgO can be separately collected by filtration. Lord (143) treats the NH_4Cl liquor from the ammonia-soda process with an amount of calcined dolomite containing just enough $Ca(OH)_2$ for quantitative reaction with the NH_4Cl in the liquor. The liberated NH_3 is expelled, and the remaining slurry is treated with CO_2 at a temperature of 60° to 80°. The MgO is thereby converted to $MgCl_2$, and the lime is precipitated as $CaCO_3$. These are separated by filtration, and the filtrate is evaporated to cause separation of NaCl. The solution is evaporated further to obtain solid $MgCl_2 \cdot 6H_2O$.

Several processes (133, 265, 414) suggest the use of $(NH_4)_2SO_4$ for the recovery of pure MgO from dolomite. Semicalcined dolomite is treated with $(NH_4)_2SO_4$ solution, and the ammonia formed is distilled off. The soluble $MgSO_4$ and insoluble $CaCO_3$ remaining are separated by filtration. The $MgSO_4$ is then treated with the NH_3 obtained in the first part of the process, producing pure $Mg(OH)_2$ and regenerating $(NH_4)_2SO_4$. Stump (289), in a similar process, treats the $MgSO_4$ solution with NH_3 in the presence of CO_2 to produce $MgCO_3$ and regenerate $(NH_4)_2SO_4$ for use in the first part of the process. Dean (424) leaches dolomite with an HCl solution of pH 6 and then treats the solution of the chlorides with $(NH_4)_2SO_4$, precipitating $CaSO_4$. The $MgSO_4$ solution is filtered off, neutralized with MgO, heated to expel NH_3, and then treated with HCl to salt out a magnesium chloride hydrate. The CO_2 from the leaching and the NH_3 from the heating are passed into an absorber, which forms $(NH_4)_2CO_3$. This solution is then treated with the $CaSO_4$ precipitate forming $CaCO_3$ and $(NH_4)_2SO_4$ for re-use in the process. Orlandi (206) heats a mixture of $(NH_4)_2SO_4$ and calcined dolomite, liberating NH_3. The sulfate is dissolved in a solution of an alkali chloride and filtered. After crystallization, the sulfate is dissolved and treated with the NH_3 generated in the first step of the process, regenerating $(NH_4)_2SO_4$ and precipitating pure $Mg(OH)_2$.

Magnesia is obtained from kieserite or other magnesium salts by adding NH_3 in the presence of water (188, 257, 259). The $Mg(OH)_2$ which precipitates is separated by flotation from the solution and the $CaSO_4$ which is formed. A German process (324) treats $MgCl_2$ with NH_3 to precipitate part of the magnesium as pure $Mg(OH)_2$, and the remaining $MgCl_2$ solution is treated wth calcined dolomite to precipitate impure $Mg(OH)_2$ for refractory purposes. Lalljee (46) and Borradaile (273) obtain anhydrous $MgCl_2$ by treating liquor containing $MgCl_2$ and $CaCl_2$ with NH_4Cl to obtain $NH_4Cl \cdot MgCl_2$, which produces $MgCl_2$ on heating. According to two German patents (362, 386) MgO can be obtained from $MgSO_4$ solutions by treating the solution with NH_3 first to precipitate $Mg(OH)_2$ and then treating the solution with SO_2 and NH_3 to precipitate $MgSO_3$. Both $Mg(OH)_2$ and $MgSO_3$ give MgO on decomposition.

Oganesyan (330) treats serpentine with a hot solution containing NH_4Cl, obtaining only nickel and magnesium in solution. These can be separated by known methods.

(6) Alkalis

(*A*) *Calcium Hydroxide:* Magnesia can be recovered from sea water and natural brines by the use of CaO or $Ca(OH)_2$ according to reaction (5).

$$MgSO_4 + MgCl_2 + 2Ca(OH)_2 \rightarrow 2Mg(OH)_2 + CaCl_2 + CaSO_4 \quad (5)$$

Many processes based on reaction (5) have been described (71, 72, 103, 105, 137, 160, 195, 216, 239, 240, 242, 254, 299, 375, 376, 377, 411). A refinement of this process is to pretreat the water in order to remove bicarbonate ions by the addition of an amount of $Ca(OH)_2$ slightly in excess of that theoretically necessary, filtering off this precipitate, and then adding the

excess $Ca(OH)_2$ to precipitate magnesia (310, 398, 419, 420). Adams (403) adds Na_2CO_3 after adding CaO in his pretreatment in order to remove calcium ions completely and to insure a pure $Mg(OH)_2$ product. Collins (418) deaerates the brine at 18° to 22° and then treats it with $Ca(OH)_2$.

Other processes (178, 182, 291, 354, 355, 356, 366) employ a different method. The sea water or brine is concentrated by evaporation, whereupon $CaCl_2$ or any soluble calcium salt is added to remove sulfate ions by precipitation. The $CaSO_4$ is filtered off, and the filtrate is further evaporated until NaCl starts to crystallize out. This is filtered off, and $Ca(OH)_2$ is added to precipitate $Mg(OH)_2$, which is recovered. The $CaCl_2$ recovered is used in the first step to precipitate the sulfate ions.

In order to prepare a purer product, Barstow (74) treats the brine with excess $Ca(OH)_2$ to precipitate all of the magnesium as $Mg(OH)_2$ and to leave the $CaCl_2$ formed in solution. After filtration, the precipitate is treated with additional brine to convert the admixed $Ca(OH)_2$ present in the precipitate to $Mg(OH)_2$ by action of the $MgCl_2$ in the excess brine. Drewsen (152) extracts $Mg(OH)_2$ from waste magnesium monosulfite liquor by boiling the liquor with powdered slaked lime.

In all of these processes, the $Mg(OH)_2$ filters very slowly. Shikin and Spiro (322) suggest the addition of tanning extract with the $Ca(OH)_2$ in order to accelerate the settling, filtration, and washing of the $Mg(OH)_2$. A German patent (339) adds an aldehyde, preferably formaldehyde, which yields a colloidal condensation product under the conditions of the process. Organic substances, such as phenol or urea, capable of forming colloidal products by reaction with the aldehyde, may also be added. An earlier French patent (332) employs a colloid but names no definite substance.

In order to precipitate a more easily filterable $Mg(OH)_2$, physical means have also been used. A recent U. S. patent (381) assigned to the Morton Salt Company describes a process in which a continuous stream of a concentrated solution of inland brine containing $MgCl_2$ is treated with a flow of finely divided solid lime. The rates of flow of brine and dry lime are controlled so that the lime is present in less than the chemical equivalent. The lime particles receive a surface film of $Mg(OH)_2$, which acts as a permeable membrane and restricts the rate at which the lime passes into liquid phase, thereby delaying the rate of reaction between the lime and the brine. The mixture is gently agitated to maintain the brine in continuous contact with the lime and to prevent breaking the $Mg(OH)_2$ crystals. The brine and lime flow through a reaction tank at a rate controlled to complete the reaction. The crystals of $Mg(OH)_2$ formed are separated from the brine.

An apparatus is described in the Chesny process (317) which delivers streams of brine and unclarified milk of lime into a reaction chamber with sufficient agitation to form but not destroy the agglomerated flocks of $Mg(OH)_2$. The stream from the reaction chamber is led into a still body of mother liquor below its surface. The $Mg(OH)_2$ produced is freed from absorbed salts by diffusion into water in a countercurrent tower process (309) and is then filtered in a special filter at high pressure.

Mastin (341) produces hydrated magnesia in a rapidly settling and readily filterable form by reaction between magnesium bitterns and lime. This process comprises gradually admixing, with a charge of granulated quicklime, an amount of bittern-carrying water sufficient for substantially complete slaking of the lime and containing about one quarter of the total amount of $MgCl_2$ required for converting the lime to magnesia. The rate of admixing is such as to maintain the mixture as a hot, plastic, steaming mass. The mixture is agitated until the lime is almost completely hydrated; then more bittern containing $MgCl_2$ in an amount sufficient to convert the remainder of the lime is gradually added to the plastic mass. The thin slurry so formed contains the $Mg(OH)_2$ in a form which can be handled easily.

Several patents (77, 86, 169) extract magnesia from ores, concentrates, residues, and similar materials by dissolving them in HNO_3 and then adding milk of lime. The $Ca(NO_3)_2$ and MgO are separated by filtration. The valuable HNO_3 may be recovered from the $Ca(NO_3)_2$ by adding H_2SO_4 to form insoluble $CaSO_4$ and HNO_3.

(*B*) *Sodium Hydroxide:* Magnesia may be obtained from silicates, dolomites, and sea water by treatment with NaOH. For extracting magnesia from silicates, Peacock (60) digests the ore with steam and NaOH to form $Mg(OH)_2$ and Na_2SiO_3, which are then separated by filtration.

For the extraction of magnesia from dolomite, Mitchell (93) treats the dolomite with NaOH or KOH at ordinary temperature. The alkali solution has a selective action on the magnesium content. The Na_2CO_3 or K_2CO_3 and $M(OH)_2$ formed are separated from the insoluble $CaCO_3$ and then from each other.

For the purification of salt solutions for the manufacture of soda, Goldshtein (321) adds NaOH in an amount insufficient to precipitate all of the magnesium and in a second stage adds NaOH and Na_2CO_3 to precipitate all of the calcium. Magnesium and calcium may be precipitated from sea water (166) in a similar manner by adding NaOH and Na_2CO_3. Larger amounts of calcium than magnesium are precipitated. Sodium carbonate precipitates a small amount of $MgCO_3$ because of the greater solubility product of $MgCO_3$. Less calcium is precipitated by NaOH above pH 10 as a result of the greater solubility of $Ca(OH)_2$ than $CaCO_3$.

In a reversal of the foregoing processes, Adams (406) treats sea water or brine with Na_2CO_3 or $MgCO_3$ and a small quantity of alkali to remove calcium and bicarbonate ions, together with suspended or colloidal iron, aluminum, and silica compounds, and then precipitates the $Mg(OH)_2$ from the sea water with an alkali solution which is free from calcium, iron, aluminum, and silica compounds.

(7) Organic Compounds

(*A*) *Acetic Acid:* A U. S. patent (149) covers the use

of acetic acid to neutralize the lime obtained from dolomite which has been calcined and slaked. The CO_2 is collected. The calcium acetate is separated by filtration, and the magnesia residue is treated with CO_2 to dissolve only the magnesia.

Acetic acid is used in dissolving dolomite selectively (1, 6, 10) to form calcium acetate in solution and leave MgO as a residue with the impurities.

(*B*) *Sugar:* One of the earliest methods of separating lime and magnesia was by means of a molasses solution. In 1881, Scheibler (7, 8) suggested its use. Since then many other men have employed this or a similar method (81, 90, 115, 194, 262, 328, 335, 368). Calcined dolomite is mixed with an impure molasses solution, which dissolves the lime as calcium sucrate but leaves the MgO unattacked. These are separated by filtration, and the MgO is recovered. The calcium sucrate is then treated with CO_2, precipitating $CaCO_3$ and leaving pure sugar in solution. The pure sugar can then be used as such or can be recycled in the system. Many of the early methods employed dolomite to purify sugar and not as a means of recovering MgO.

Wedding (13), using this method, obtains a product containing 95.99% of MgO and 2.18% of CaO with a molasses loss of from 5 to 10%. He says this loss is too large to be economical but states that the qualities of refractory brick made from magnesia recovered in this manner are exceptionally good. On the other hand, Liberman (300) shows by economic data that the efficiency of the process is entirely satisfactory.

Because only the lime in the dolomite is soluble in the sugar, the MgO obtained is almost always contaminated with impurities such as Fe_2O_3, SiO_2, and others. Hart (361, 382) prepares a pure product from this MgO by suspending the residue from the sucrate solution in water and then carbonating it until soluble $Mg(HCO_3)_2$ is formed. This bicarbonate is filtered from the impurities, which are left in an insoluble state by the carbonation. The $Mg(HCO_3)_2$ solution is then converted to pure MgO by heating and calcining.

Kutzev and Kruzman (263, 287, 288) employ molasses in a slightly different way. The calcined dolomite is treated with molasses at 0° to 15°. Insoluble calcium trisucrate is formed along with the MgO. These are separated from the nonsugar substances by filtration. The calcium trisucrate is then treated with additional sugar solution to form soluble calcium mono- and di-sucrate. These soluble sucrates are filtered off leaving MgO. The sugar may be recovered from the sucrates by treating the solution with CO_2.

(8) Sea Water

If a slurry of calcined dolomite is added to sea water, $Mg(OH)_2$ is precipitated from the solution (329, 334, 392). A German firm (214) controls the amount of dolomite added so that the amount of CaO in the dolomite is equivalent to the $MgCl_2$ present in the solution; then heats the mixture. Chesny and Elkington (409) have patented a method whereby a slurry of calcined and slaked dolomite is sprayed obliquely onto the surface of a moving body of sea water. Because of the impact of the droplets of slurry on the surface of the water, very thin platelike aggregates of precipitate are formed. Rapid diffusion of the convertible magnesium salts contained in the sea water takes place through the platelike aggregates and the $Ca(OH)_2$ reacts completely with the magnesium salts without the necessity for breaking up the crystal aggregates.

Sisson (17, 24) treats calcined dolomite with sea water until all of the CaO in the dolomite is converted to $CaCl_2$. Half of the resulting slurry is then treated with CO_2 until the magnesia is converted to bicarbonate. The bicarbonate is filtered off and added to the other half of the slurry to precipitate $MgCO_3$. Richards (134) treats undecomposed magnesite with sea water, removing impurities such as calcium and silica and recovering pure $MgCO_3$.

(9) Electrochemical Methods

One of the methods of obtaining MgO from sea water and brines is to pass the liquid through the cathode compartment of a cell (345, 350, 353). By controlling the current density and potential, $Mg(OH)_2$ can be precipitated. The $Mg(OH)_2$ can then be dried and roasted to give pure MgO.

In an early German patent (33), the end liquors in the manufacture of potash are subjected to electrolysis; $Mg(OH)_2$ appears at the cathode. The $Mg(OH)_2$ collects on the bottom of the cell; and if it is left for some time in the electrolyte, it is converted to the oxychloride. This mixture of hydroxide and oxychloride is removed from the electrolyte and heated to a high temperature without preheating. This treatment produces HCl gas and a residue of MgO.

Delage (80) obtains MgO from dolomite by melting dolomite with $NaHSO_4$ and then treating this mixture with water while hot. The solution is electrolyzed with a controlled current density and potential. The acid produced is neutralized by circulating the anode liquid over dolomite, filtering, and returning the liquid to the cathode compartment. The MgO formed is filtered from the electrolyte, dried, and calcined. A French patent (73) similarly describes the production of MgO by the electrolysis of mixed sulfates. Allen (198) recovers magnesia from dolomite by electrolyzing a slaked solution of calcined dolomite.

(10) Ion Exchange

One of the newer methods of obtaining soluble magnesium salts is that of ion exchange covered in a series of patents assigned to Ocean Salts, Ltd. A solution containing mixed soluble magnesium salts is passed through organic cation-exchange material, whereby the magnesium ions are absorbed by the material. A solution of H_2SO_4 is then passed through the material to produce a solution of $MgSO_4$, which in turn is collected and neutralized (399). Another patent (408) recommends treating the exchange material containing the magnesium ions with a solution of a chloride to produce $MgCl_2$. Another process (415) brings $MgCl_2$ in sea water in contact with a cation-exchange material, producing HCl and leaving magnesium ions in the material. The HCl is then passed through an

alkali-treated, anion-exchange medium leaving the material with chloride ions. This material is treated with $Mg(OH)_2$ in suspension yielding pure $MgCl_2$ in solution. The original cation-exchange material containing the magnesium ions is treated with H_2SO_4 to produce pure $MgSO_4$ in solution.

(11) Miscellaneous Chemical Methods

Clarke (42) makes $MgSO_4$ by adding finely pulverized dolomite to a hot aqueous solution of $FeSO_4$ in less than the amount necessary to combine with the $FeSO_4$. Sufficient pulverized MgO is added to complete the combination, the solution is agitated, and the precipitated $Fe(OH)_2$ is filtered off. The $CaSO_4$ and $MgSO_4$ are then separated by fractional crystallization.

A British patent (364) suggests the separation of MgO from calcined dolomite by lixiviation with excess phenolic reagent and a solvent. The lime is removed as a soluble phenolate while the MgO remains in the sludge.

Adams (407) treats sea water or brine with a soluble silicate to precipitate the magnesium ions. The calcium ions present in the water are removed by treatment before the precipitation of the magnesium ions. An excess of soluble silicate is avoided to prevent the formation of colloidal magnesium silicate and to insure the production of a product that will settle rapidly.

In another patent, Adams (412) precipitates MgF_2 directly from sea water, brines, and the like by the addition of a soluble fluoride.

IV. Miscellaneous

A number of surveys (130, 156, 158, 281, 284, 326, 358, 359, 360, 417, 429) have been made to determine the feasibility of commercial processes for producing magnesia. These surveys include studies of costs, purity of the product, value of by-products, and availability of the reagent.

Part B of the bibliography, Nos. 432 to 461, inclusive, includes patents and articles dealing with the extraction of magnesia from magnesium-bearing raw materials. Because no detailed information on these references is available to the writers, they have not been included in the text.

V. Conclusions

This survey of the literature reveals that there are many methods of recovering magnesia from dolomite and other magnesium-bearing raw materials. For refractory purposes, a magnesia product that contains approximately 90 to 92% of MgO, 5% of SiO_2, and the remaining lime, alumina, and iron is preferable in commercial practice to a highly refined magnesia. This product can be obtained most economically in large volumes by a combination of chemical and physical methods. Among the most popular processes of this type are those in which sea water or brine is treated with lime or calcined dolomite.

Magnesia for medicinal and chemical purposes, however, must be of high purity and must possess certain physical properties which are dependent on its use. Chemical processes alone are therefore preferred for manufacturing magnesia of this type because the purity and the physical properties can more easily be controlled. Among the more popular chemical methods of recovering pure magnesia are those which treat slaked calcined dolomite with CO_2.

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REACTIONS IN SOLID STATE: III, REACTION BETWEEN SODIUM CARBONATE AND QUARTZ*

By George Gibson† and Roland Ward

Abstract

Reactions of sodium carbonate with quartz occur without fusion between 726° and 805°C. When the reactions are conducted in a stream of nitrogen, the size of the charge, composition of the mixture, rate of flow of gas, and duration of reaction have appreciable effect on the reaction rates and on the nature of the product.

In presence of sufficient sodium carbonate, the end product of the reaction at the higher temperatures is the orthosilicate. The formation of a series of silicate ions as intermediate products between the metasilicate and the orthosilicate by interaction of the former with carbonate ions is postulated. This process is considered to be reversible with the smaller silicate ions. This theory, moreover, serves to reconcile several apparent anomalies in the experimental data.

The rate of reaction of the silica particle is not measured by the rate of carbon dioxide evolution.

I. Introduction

The system Na_2O–SiO_2 has been investigated, revealing in the solid phase the existence of the compounds $2Na_2O \cdot SiO_2$, $Na_2O \cdot SiO_2$, and $Na_2O \cdot 2SiO_2$. Kracek[1] gives the melting points of these compounds. Although Kröger and Fingas[2] have postulated the existence of the trisilicate, $Na_2O \cdot 3SiO_2$, it has been shown‡ that the glass of this composition, on complete devitrification, yields the disilicate and quartz. Kröger and Fingas studied the equilibrium pressure of mixtures of alkali carbonates and quartz and also of various alkali silicates with the corresponding alkali carbonates. They conclude that the so-called trisilicate reacts with excess sodium carbonate at 900°C. to give the metasilicate which reacts further to give the orthosilicate. With the lithium compounds, the reaction progressed to the formation of $Li_{8(0)}SiO_{4(3)}$.

In the solid-phase reaction of sodium carbonate with quartz, the metasilicate is the usual product reported, although Howarth, Maskill, and Turner[3] suspected the formation of the orthosilicate at temperatures above 700°C. They investigated the kinetics of the reaction of quartz particles (150- to 180-mesh) and sodium carbonate in the mol ratios of SiO_2 to Na_2CO_3 from 1 to 4. More rapid decomposition of the sodium carbonate was effected with higher mol ratios, and it was roughly proportional to the surface area of the quartz. The rate was found to be of first order.

Similar investigations were carried out by Pole and Taylor,[4] who used a static method for following the reaction rates. Rather limited reactions were obtained between 702° and 758°C. The percentage reaction was referred to the complete decomposition of the sodium carbonate, but the nature of the reaction product was not given. The parabolic law, expressed in Jander's equation, $(1 - \sqrt[3]{1-\alpha})^2 = Kt$, was thought to be applicable, although the value of $K \times 10^4$ decreased steadily from 0.67 at 2% of reaction to 0.085 at 10.2% of reaction.

The reaction of barium carbonate with silica was used by Jander[5] to illustrate the validity of his theory. Mixtures containing excess of barium carbonate gave the orthosilicate, whereas those containing excess of silica gave the metasilicate. These reactions were studied over a rather limited range. Serin and Ellickson[6] have used these data to show that the reaction rates conform somewhat better to equation (1).

$$1 - \alpha = \frac{6}{\pi^3} \sum_n \frac{1}{n^2} \exp. - \frac{n^2 \pi^2 D t}{R^2} \qquad (1)$$

The extent of reaction of the silica was small in all of the solid-phase reactions of silica so far reported. None of the mixtures contained enough sodium carbonate to carry the reaction to completion with the formation of the orthosilicate. The present study has been extended to cover the range between the metasilicate and the orthosilicate. It was also necessary to examine some of the factors involved in the measurement of reaction rates using the flow method.

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† Abstracted from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1942; Dr. Gibson is now located at the Illinois Institute of Technology, Chicago, Ill.

[1] F. C. Kracek, "System Sodium Oxide–Silica," *Jour. Phys. Chem.*, **34** [7] 1581–98 (1930); p. 1583; *Ceram. Abs.*, **9** [10] 881 (1930).

[2] Carl Kröger and Ernst Fingas, "Action of Quartz and Alkali Silicates on Alkali Carbonates," *Z. Anorg. Allgem. Chem.*, **213** [1] 12–57 (1933); *Ceram. Abs.*, **14** [1] 21 (1935); *Chem. Abs.*, **27** [19] 4751 (1933).

‡ F. C. Kracek, Geophysical Laboratory, Washington, D. C., personal communication.

[3] J. T. Howarth, W. Maskill, and W. E. S. Turner, "Rate of Reaction Between Silica and Sodium Carbonate at Different Temperatures and Processes of Vitrification," *Jour. Soc. Glass Tech.*, **17**, 25–49T (1933).

[4] G. R. Pole and N. W. Taylor, "Kinetics of Solid-Phase Reaction of Certain Carbonates with Mullite, Silica, and Alumina," *Jour. Amer. Ceram. Soc.*, **18** [11] 325–37 (1935).

[5] Wilhelm Jander, "Reactions in Solid State at High Temperatures: I, Reaction Rates of Endothermic Reactions," *Z. Anorg. Allgem. Chem.*, **163**, 1–30 (1927).

[6] B. Serin and R. T. Ellickson, "Determination of Diffusion Coefficients," *Jour. Chem. Phys.*, **9**, 742–47 (1941); *Chem. Abs.*, **35** [22] 7782 (1941).

II. Experimental

The upper temperature limit found for solid-phase reactions with the mixtures used was about 800°C. Even at this temperature, very slow reactions were obtained with quartz of large particle size such as may be obtained by screening. Fairly uniform quartz samples were obtained by elutriating quartz sand ground to pass a 325-mesh screen. Two samples containing uniform particles were obtained, one with particles of mean diameter of 5 to 7 microns and the other of 2 to 3 microns. Many of the data reported were obtained by using the ground quartz which passed 325-mesh screen. Mixtures of this quartz with sodium carbonate were made in a roller mill, whereas the mixtures containing uniform quartz were made by hand mixing. Analysis showed all of the samples to be reasonably uniform. The composition of these mixtures and their designating symbols are listed in Table I.

TABLE I

COMPOSITIONS OF MIXTURES AND THEIR SYMBOLS

Quartz sample (size)	Mol ratio of Na_2CO_3/SiO_2	Symbol
325-mesh	1	A_1
" "	2	A_2
" "	2.5	A_3
5–7 μ	1	B_1
	2	B_2
2–3 μ	2	C_2

Reaction rate studies were made with these mixtures at four temperatures between 726°C. and 792°C., the rates being measured by the evolution of carbon dioxide. The apparatus was similar to that previously described[7] except that the temperature of the furnace was controlled within 0.1° by a thyratron circuit devised by Waring and Robison.[8] The short temperature range and the long duration of the runs demand such a control. The flowmeter was capable of measuring accurately between 25 and 630 ml. per min.

Commercial tank nitrogen was used in all of the runs. The platinum boat was placed in the furnace in contact with the thermocouple, and 10 to 15 minutes were required for the boat to reach furnace temperature. An analysis of each product was made to determine the extent of the reaction of the silica.

(1) Influence of Size of Sample on Reaction Rate and Reaction Product

Four samples of mixture A_2 were used in this experiment.

The smallest charge that would give sufficient carbon dioxide for reasonable precision and sufficient product for analysis was about 0.7 gm. The capacity of the boat set the upper limit. The data obtained are given in Table II. The rate of flow of nitrogen was maintained in all cases at 125 ml. per min. throughout the reaction. The ratio of Na to Si in the product was calculated from the loss in weight of the samples and the water soluble silicate. The silicate analyses checked within 1%.

TABLE II

INFLUENCE OF SIZE OF CHARGE ON REACTION PRODUCT AND REACTION RATE

Mass of sample (gm.)							
0.713		1.5000		2.7000		3.3946	
Silica decomposed (%)							
74.7		75.9		68.2		68.6	
CO_2 evolved (%)							
66.1		60.2		55.9		53.2	
Ratio of Na/Si in product*							
3.54		3.17		3.27		3.10	
Rate of evolution of CO_2†							
t	x	t	x	t	x	t	x
0.75	16.7	1.0	18.0	1.0	18.1	1.0	16.7
2.25	24.0						
11.75	47.1	10.5	39.7	12.0	35.7	12.0	33.1
35.75	57.7	22.5	49.5	24.5	44.6	23.5	41.2
38.0	64.6	34.5	56.1	37.0	53.2	36.0	49.6
46.0	69.1	47.5	60.6	45.0	56.1	47.5	53.8

* Calculated from loss in weight of sample.
† t = time (hr.); x = CO_2 (%).

The data show that the extent of reaction of the sodium carbonate and of the silica is affected. In the case of sodium carbonate, the increase in percentage reaction with decreasing mass of charge is linear for the first three points, but a more rapid reaction is obtained with the smallest charge. The increase in the extent of reaction of the silica is more irregular, but it is almost linear.

A plot of x against t shows that the initial reaction is about the same for all samples. The difference, however, is most pronounced in the period from one to twelve hours.

A marked difference occurs in the ratio of Na to Si only for the smallest charge.

(2) Influence of Rate of Flow of Nitrogen on Reaction Rates and Reaction Products

These tests were carried out at 770°C., using flow rates of nitrogen of 50 to 500 ml. per min. Mixtures A_1, A_2, and B_2 were used. Five samples of A_1, weighing about 3.3 gm., were heated for 21.5 hr. The carbon dioxide evolved was determined by the loss in weight, and no kinetic data were recorded. With mixtures A_2 and B_2, using 3-gm. samples, the rate of evolution of carbon dioxide was measured at all flow rates up to 300 ml. per min. Mixture A_2, at a flow rate of 500 ml. per min., was treated in the same manner as the A_1 mixtures.

The data recorded in Tables III and IV show that the rate of flow of nitrogen has considerable influence on the rate of evolution of carbon dioxide but that it is not the same for all mixtures.

Some difference may be noted in the reaction of the silica in the A_1 mixtures. Although the extent of

[7] R. Ward and J. D. Struthers, "Reactions in Solid State: I, Reactions Between Barium Carbonate and Ferric Oxide in Presence of Oxygen," *Jour. Amer. Chem. Soc.*, **59**, 1849–54 (1937); *Chem. Abs.*, **31** [22] 8331 (1937).

[8] C. E. Waring and G. Robison, "Experimental Details for Precision High-Temperature Control Utilizing the Hull Circuit," *Rev. Sci. Instruments*, **14**, 143 (1943).

TABLE III

INFLUENCE OF FLOW RATE OF NITROGEN ON REACTION RATE AND PRODUCT

Flow rate (ml./min.)	CO_2 (%) evolved: At 21.5 hr.	CO_2 (%) evolved: At end	Soluble SiO_2 (%) at end of reaction	Na/Si in product
		Mixture A_1		
50	55.7		50.2	2.2
100	58.7		48.9	2.4
150	62.8		43.2	3.0
300	69.2		46.9	3.0
500	72.8		48.1	3.4
		Mixture A_2		
50	31.5	35.3	68.7	3.2
200	43.0	55.8	69.4	3.3
300	45.0	63.4	75.9	3.3
500	44.2		54.3	3.3
		Mixture B_2		
50	46.0	76.5	92.8	3.3
300	56.0	81.2	97.0	3.4

TABLE IV

EFFECT OF FLOW RATE OF NITROGEN ON REACTION RATE

Time (hr.)	Mixture A_2 (flow rate): 50	200	300	Mixture B_2 (flow rate): 50	300
1	16.0	15.6	16.6	18.8	21.8
5	22.5	23.3	26.0	30.0	28.0
10	26.5	30.3	34.0	36.0	39.0
20	32.0	41.0	44.0	45.0	55.0
30	37.8	48.5	50.0	52.0	65.0
40	43.0	53.0	54.0	58.5	71.0
50	48.0	55.0	57.0	64.0	74.6
60	52.0	56.0	60.3	69.0	77.5
70	54.8		63.3	72.2	79.5
80				74.0	80.9
100				75.0	
120				76.0	

reaction of the sodium carbonate increases with increasing flow rate, the silica shows a decrease in reaction from 50 to 150 ml. per min. and then an increase to 500 ml. per min.

The ratio of Na to Si in the products from the A_1 mixtures increases with flow rate, whereas little change is seen in that for the A_2 products. At the highest flow rates, the ratio is nearly the same for products from both mixtures.

A plot of x against t from the data in Table IV reveals the fact that, at 50 ml. per min., a linear relationship holds from about 10 to 50 hr., whereas the slope of the curve decreases over the whole reaction range at 300 ml. per min. The effect of the rate of flow of nitrogen is greatest after the initial rapid reaction is over.

(3) Influence of Duration of Reaction on Nature of Product

The samples were heated at constant temperature for different periods of time. With the A mixtures, the rate of flow of nitrogen was 50 ml. per min.; with the B_2 mixture, 300 ml. per min. (see Table V). Kinetic data were also obtained for the latter mixture. The percentage of carbon dioxide is calculated from the decrease in weight of the samples. The weights of all A mixtures were between 3.5 and 4.0 gm., and

TABLE V

EFFECT OF DURATION OF REACTION ON NATURE OF PRODUCT

Mixture	Duration (hr.)	CO_2 evolved (%)	Soluble SiO_2 (%)	Na/Si in product
		Temp. 771°C.		
A_1	1	27.4	23.8	2.3
	21.5	55.7	50.2	2.2
	110	72.0	66.0	2.2
A_2	2	18.0	34.4	2.1
	44.5	41.8	62.0	3.0
	167.3	50.3	72.2	2.8
A_3	3.5	20.0	45.0	2.2
	50.5	41.8	64.2	3.3
	144	44.2	75.0	3.0
B_2	5	30.4	56.9	2.1
	30	67.4	86.1	3.2
	81	81.2	97.0	3.4
		Temp. 798°C.		
A_3	48.5	39.2	83.2	2.4
	111	68.8	88.5	3.9
		Temp. 805°C.		
A_1	11	88.0	87.8	2.0
	47.5	98.0	91.4	2.1
A_2	23	70.9	91.1	3.1
	128	80.9	88.9	3.7

these did not differ by more than 0.1 gm. for the same mixture at the same temperature. In the case of the B_2 mixture, 3-gm. samples were used. The products obtained from the A_1 mixture obviously do not change appreciably from 1 to 110 hr. at 771°C. or from 11 to 47.5 hr. at 805°C., but the mixtures containing a larger proportion of sodium carbonate yield products which show an increase in the ratio of Na to Si with time. The A_2, A_3, and B_2 mixtures give comparable results in spite of the different conditions. The A_2 and A_3 mixtures at 771°C. show an appreciable decrease in ratio on prolonged heating. An apparently anomalous product is obtained with the A_3 mixture after 48.5 hr. at 798°C. when the ratio is found to be less than that obtained after 50.5 hr. at 771°C. The general tendency, however, seems to be toward an increase in the ratio with rising temperature.

(4) Influence of Temperature Change on Reaction Rate and Reaction Product

Reaction rate measurements were made on the B_1 and B_2 mixtures at 726°, 749°, 771°, and 792°C. In all tests, 3-gm. samples and a flow rate of 300 ml. per minute were used. The reactions were continued until the rate of evolution of the carbon dioxide was less than 4 mg. per hr.

Table VI gives the kinetic data. Except for the first two and the last points, the values listed were interpolated from a curve drawn through the eperimental points. About the same number of readings were taken as are listed in Table VI. Some idea of the reproducibility of the data may be obtained from Table VII, which represents two shorter runs with mixture B_2 at 771°C. The maximum deviation from a smooth curve drawn through the points is less than 2%. The analytical data for the products from these runs are given in Tables V and VIII. The rate of reaction

TABLE VI

KINETIC DATA

Time (hr.)	CO_2 (%) evolved at 726°C.	749°C.	771°C.	792°C.
	Mixture B_2			
0.5	10.5	13.7	16.3	26.3
1.0			18.8	31.6
1.5	13.1	18.4		
5.0	20.0	25.5	32.5	54.0
10.0	26.0	33.0	43.0	65.5
20.0	36.0	44.0	56.5	73.5
30.0	42.5	53.5	65.5	77.0
40.0	48.0	62.0	71.0	79.5
50.0	53.0	67.3	75.0	81.5
81.0	65.0	75.0	81.0	87.2
96.5	69.5	77.0		89.5
137.0	76.3	82.4		
169.0	78.4			
	Mixture B_1			
0.5	16.3	19.8	25.4	39.0
1.0		23.3	30.1	43.5
1.5	20.5			
2.0	23.0	30.0	36.5	59.0
5.0	32.0	40.5	49.0	77.0
7.5	38.0	47.0	57.0	87.0
12.5	47.0	57.1	71.0	98.0
16.0	52.5	63.0	79.0	100.0
21.0	59.1	70.2	88.0	100.1
28.0	67.0	79.0	96.8	
36.0	74.8	87.5		
48.5	83.0	97.6		
55.0	86.2			

of the sodium carbonate increases, as should be expected, with increasing temperature, but the behavior of the silica is anomalous. With the B_2 mixture, the extent of reaction of the silica after 81 hr. at 771°C. is greater than that obtained after 96.5 hr. at 792°C. This difference is far beyond the experimental error. The conditions do not permit a similar comparison of the data obtained with the B_1 mixtures. The increase in the ratio of Na to Si, however, seems to be much greater in the first temperature interval than n the others.

(5) Influence of Particle Size of Quartz on Reaction Rate

A limited amount of mixture C_2 was available. An attempt was made to compare the reaction rate for this mixture with that for mixture B_2 at 726°C. The temperature control unfortunately failed to operate after 48.5 hr. The kinetic data up to this point are given in Table IX.

III. Interpretation of Results

(1) Nature of Product in Relation to Experimental Conditions

The formation of silicate ions from quartz must involve the rupture of Si–O bonds in the continuous network of the quartz lattice. Two types of silicate ion may be produced, namely, the chain type, for which the general formula $Si_nO_{3n+1}^{-2(n+1)}$ may be written, and the ring type $(SiO_3)_n^{-2n}$. The most usual values for n in the ring type would be 3, 4, or 6. This type corresponds exactly to the metasilicate empirical

TABLE VII

DATA FOR TWO SHORTER RUNS WITH MIXTURE B_2 AT 771°C.

Time (hr.)	CO_2 (%)	
0.5	16.7	15.8
1.0		18.5
1.5	21.8	
2.0		22.0
3.0		25.3
3.5	27.3	
5.0		30.4
6.5	33.4	
12.0	44.1	
24.0	63.0	
30.0	68.4	

TABLE VIII

ANALYTICAL DATA FOR PRODUCTS OF SHORTER TESTS

Temp. (°C.)	CO_2 evolved (%)	Soluble SiO_2 (%)	Na/Si in product
	Mixture B_2		
726	77.3	91.0	3.4
749	81.6	91.3	3.6
771	81.2	97.0	3.4
792	88.9	91.2	3.9
	Mixture B_1		
726	85.6	75.3	2.3
749	95.7	67.7	2.8
771	95.7	63.8	3.0
792	100.0	65.5	3.1

TABLE IX

KINETIC DATA

Mixture C_2 at 726°C.			
t (hr.)	CO_2 (%)	t (hr.)	CO_2 (%)
0.25	22.1	12.0	43.0
0.75	23.7	24.5	51.7
1.5	25.9	36.0	58.5
3.5	30.6	48.5	63.1

formula, $M^I_2SiO_3$, whereas the chain type approaches the metasilicate formula only at large values of n. None of these ions would produce a compound having a Na to Si ratio greater than 4 or less than 2. It is conceivable, however, that small portions of the quartz lattice may be isolated in an interfacial reaction to give a colloidal particle whose surface carries the ion charge. The Na to Si ratio here could be much less than 2. There is also the possibility of the formation of amphibole-like ions or disilicates.

Values of the Na to Si ratio greater than 2 and less than 4 may be taken to indicate a mixture of silicate ions. If the value is greater than 3, the orthosilicate must be present, and the larger the accompanying ions the greater the percentage of orthosilicate. Ratios of exactly 3 or less could be explained in a similar fashion with the $Si_2O_7^{-6}$ as the simplest ion present, but there is always the possibility of the presence of the orthosilicate.

The largest Na to Si ratio obtained was 3.9. This product must contain at least 90% of orthosilicate if all the remaining silica is in the form of the $Si_2O_7^{-6}$ ion. The lowest ratio found in any product was 2.0 with the A_1 mixture at 805°C. (Table V), which suggests the formation of one of the metasilicates or a mixture of

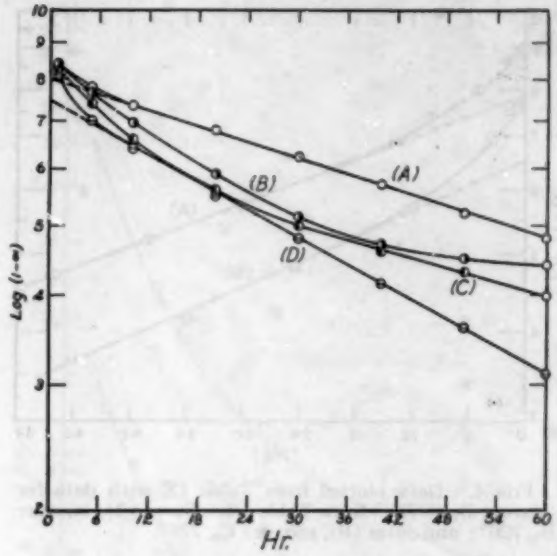


FIG. 1.—Data plotted from Table IV. *Curve* (*A*), mixture A_2, 50 ml. per min.; *curve* (*B*), mixture A_2, 200 ml. per min.; *curve* (*C*), mixture A_2, 300 ml. per min.; and *curve* (*D*), mixture B_2, 50 ml. per min.

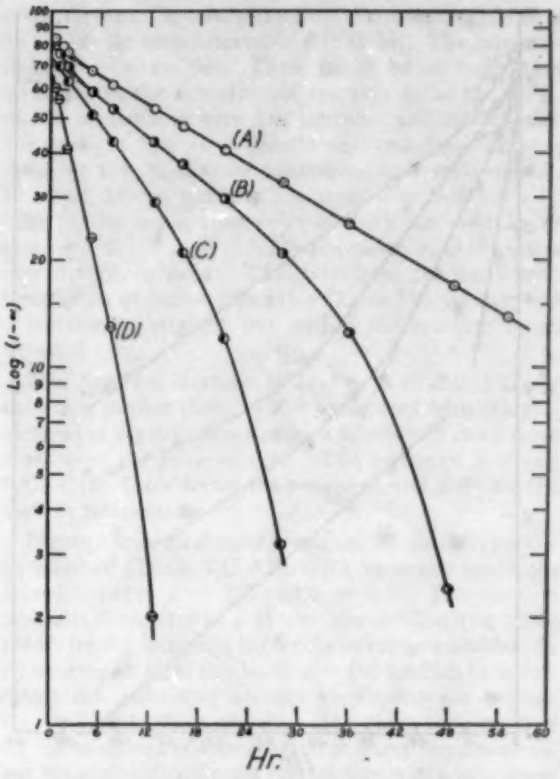


FIG. 2.—Data for mixture B_1 taken from Table VI. *Curve* (*A*), 726°; *curve* (*B*), 749°; *curve* (*C*), 771°; and *curve* (*D*), 792°.

them. There is also the possibility of a fortuitous mixture of disilicates, trisilicates, etc., and of simpler silicates. Inasmuch as no ratio was found to be less than 2 even in the early stages of the reaction, the latter possibility seems unlikely.

The following mechanism is suggested for the formation of the silicate ions:

(1) The ionic process involved is the reaction of the carbonate ion with the Si–O–Si linkage at the quartz crystal surface.

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + CO_3^{=} \rightarrow -\overset{|}{\underset{|}{Si}}-\bar{O} + \bar{O}-\overset{|}{\underset{|}{Si}}- + CO_2 \qquad (2)$$

Further penetration of carbonate ions will lead to the isolation of a complex silicate ion. The ring type is a distinct possibility because the silicon atoms have a spiral arrangement, but the rupture of the rings or the production of long chains appears to be equally probable.

(2) The carbonate ions must diffuse through this initial product and may react with silicate ions en route, according to the general equation (3).

$$Si_nO_{3n+1}^{-2(n+1)} + xCO_3^{=} \longrightarrow \frac{n}{x}\,Si_xO_{3x+1}^{-2(x+1)} + xCO_2 \qquad (3)$$

The degradation of the long-chain silicate ion would be complete when the orthosilicate ion ($x = 1$) is reached. If it is assumed that a higher activation energy is required to separate the end SiO_4^{-4} tetrahedra as a result of the greater negative charge in that region, it follows that the most likely immediate product would be a mixture of $Si_2O_7^{-6}$ and $Si_3O_{10}^{-8}$ with a smaller number of orthosilicate ions. The proportion of orthosilicate ions, moreover, would be increased with rising temperature. An equimolar distribution of SiO_4^{-4} and $Si_2O_7^{-6}$ ions would give a Na to Si ratio of 3.33. The ratio 3.3 to 3.4 was found frequently in the reaction products at 771°C. At higher temperatures and with the mixtures containing the higher proportion of sodium carbonate, more orthosilicate was formed (see Tables III and V).

(3) These reactions are reversible in the sense that larger ions may be built up according to equation (4).

$$2Si_xO_{3x+1}^{-2(x+1)} + CO_2 \longrightarrow Si_{2x}O_{6x+1}^{-2(2x+1)} + CO_3^{=} \qquad (4)$$

It is thought unlikely that the quartz lattice would be regenerated to any extent by this process. The equilibrium studies by Kröger and Fingas[2] support this hypothesis. Although they claim that the equilibrium $Na_2CO_3 + SiO_2 \rightleftharpoons Na_2Si_2O_5 + CO_2$ was obtained, the present writers believe that the interpretation given in equation (4) could be given to their data. The reaction with the carbon dioxide would become more usual the smaller the value of x.

Any process which hindered the desorption of the carbon dioxide from the surface of the reaction block would thus tend to increase the chain length of the silicate ion. The data in Table II, showing the effect of decreasing weight of charge, support this point. The increase of surface per unit mass of charge helps to liberate carbon dioxide, and the average chain

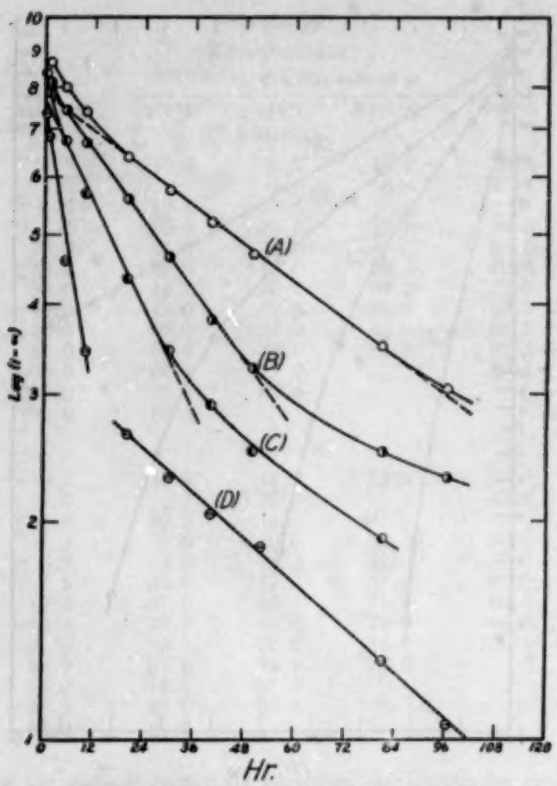
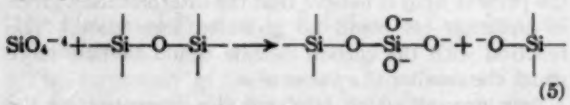


FIG. 3.—Data for mixture B_2 taken from Table VI. *Curve* (*A*), 726°; *curve* (*B*), 749°; *curve* (*C*), 771°; and *curve* (*D*), 792°.

length decreases from a value close to 2 to 1.33. The data showing the influence of flow rate on the reaction also lend some support to this theory. Only a slight decrease in average chain length is observed with the A_2 and B_2 products from 50 ml. per minute to higher ratio of flow. With the A_2 mixtures, the change is from 1.66 to 1.54; with the B_2 mixtures, it is 1.54 to 1.43.

With the A_1 mixture, however, the influence is shown over the entire range; at 50 ml. per min., x equals 10; at 500 ml. per min., x equals 1.43. At the same flow rate, the value of x is always greater for the 1 to 1 mixtures than for the 2 to 1 mixtures (see Tables III, V, and VIII). The chance of desorption of the carbon dioxide seems likely to be greater from the surface of the mixtures richer in sodium carbonate.

(4) There is also the possibility that the quartz could react with silicate ions in a manner suggested by equation (5).



(5)

The rate of reaction of the quartz depends on the penetration of the carbonate ions to its surface and to some extent also on the reaction with the silicate ions.

The percentages of soluble silica in the products from the A_1 mixture shown in Table III are strictly comparable. A decrease occurs at first while the chain

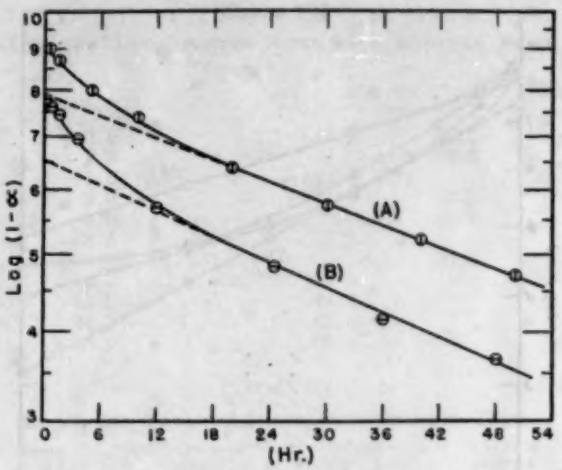


FIG. 4.—Data plotted from Table IX with data for mixture B_1 at 726° from Table VI. *Curve* (*A*), mixture B_2, 726°; and *curve* (*B*), mixture C_2, 726°.

length decreases from 10 to 3. This decrease is thought to be the result of the removal of carbonate ions according to reaction (3), in which the disilicate and orthosilicate ions produced at the quartz surface cause further reaction with the quartz. The carbonate and silicate ions both attack the quartz. A similar explanation may be sought for the data in Table VIII, which show that the reaction of the quartz is greater after 81 hr. at 771°C. than after 96.5 hr. at 792°C. In the latter reaction, the carbonate ions may be assumed to be efficiently screened out in the formation of the orthosilicate ion. This product contains at least 90% of orthosilicate. The decrease in reaction of the silica with rising temperature of the B_1 mixtures shown in Table VIII, however, cannot be used to justify this mechanism because the reaction time was progressively shorter.

From these considerations, the sodium carbonate-quartz reaction is shown to be fairly complicated. It will be necessary to know the extent of reaction of the silica at all stages of the reaction.

The existence of these silicate ions in the reaction products may not be capable of direct demonstration unless the formation of a distinct solid phase of appropriate composition could be observed by a phase-equilibrium diagram or by X-ray diffraction. The formation of a solid phase is a function of the cation as well as of the anion.

(2) Reaction Rates of Sodium Carbonate

From the discussion of the nature of the product and from the experiments which showed the influence of flow rate and size of charge on the reaction rates of the various mixtures, it may seem absurd to attempt to interpret the kinetic data on the basis of the simple theories of reaction rates of solids. This interpretation may be the more confusing because the theories under consideration are based on the reaction of spherical uniform particles. The uniform particles in the B and C mixtures are the quartz particles whose reaction

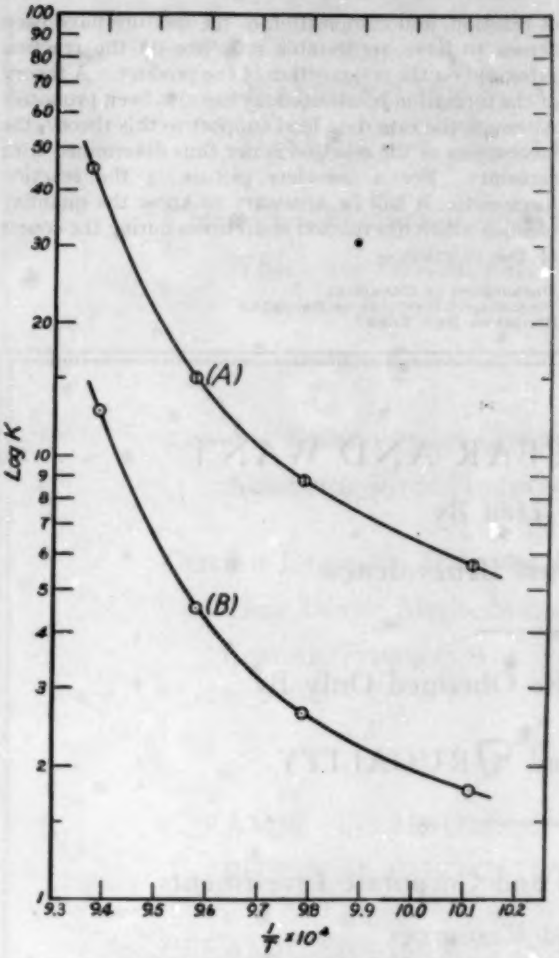


FIG. 5.—Data for mixture B_1 and B_2. *Curve* (*A*), mixture B_2; and *curve* (*B*), mixture B_1.

rates are not known and cannot be calculated with any degree of certainty because the product does not always remain the same during the run. Some interesting information may nevertheless be obtained.

One of the authors in a previous publication[9] has suggested that a plot of log $(1 - \alpha)$ against time (α = percentage of reaction/100) might reveal the nature of the reaction mechanism. A straight line through the origin over the entire reaction indicates a first order reaction. If the rate becomes greater after about 80% of reaction, an interfacial unimolecular reaction is the process, whereas a straight line obtained after 30 to 70%, whose intercept on the ordinate lies between $(1 - \alpha) = 0.6$ and $(1 - \alpha) = 0.8$, indicates a diffusion controlled reaction.

Figure 1 shows the data from Table IV plotted in this manner. With the slowest rate of flow, the A_2 and B_2 mixtures agree fairly well with the predictions of equation (1). In the case of the A_2 mixture in which the silica particles are not uniform, the experimental points lie on a straight line from $\alpha = 0.23$ to $\alpha = 0.52$ in the time interval of 6 to 60 hr. The intercept is at $(1 - \alpha) = 0.8$. There might be an inclination to interpret the initial rapid reaction to be the result of the presence of very fine particles and to attribute the straight line to a pseudo first-order mechanism; data for the B_2 mixture containing uniform particles, however, give a straight line from $\alpha = 0.30$ to $\alpha = 0.69$ in the same time interval with an even lower intercept $(1 - \alpha = 0.74)$. The slope in this case is considerably greater. The data from the tests with mixture A_2 at higher flow rates (Table IV) do not yield a convincing straight line within the reaction range covered.

The data for mixture B_1 in Fig. 2 (Table VI) are used in a similar plot. A fair agreement with the predictions of the diffusion equation is obtained in all cases from $\alpha = 0.3$ to $\alpha = 0.85$. The intercept is about 0.8 for the three lower temperatures and 0.67 for the highest temperature.

Figure 3 shows a similar treatment of the data for the B_2 mixture (Table VI). Straight lines are again obtained between $\alpha = 0.3$ and $\alpha = 0.7$. The reaction proceeds thereafter at a slower rate in all cases. The points for the foregoing highest temperature reaction lie on another straight line up to $\alpha = 0.89$, which indicates rather definitely that another mechanism has become the rate controlling process. The same may be true for the reactions of this mixture at lower temperatures, but the reactions were not carried far enough to confirm this supposition.

The data in Table IX are plotted in Fig. 4 along with the data for the B_2 mixture at 726°C. from Table VI. The particle size is in the ratio of 1 to 2.4. The diffusion equation requires that the slope should be about six times greater for the reaction of the smaller particles whereas the intercept should be the same. It may be seen that the slopes are similar, but that the intercept is much lower in the case of the mixture with the smaller particles. It seems more likely, therefore, that the initial rapid reaction (the lowering of the intercept below $(1 - \alpha) = 1$) is the result of a contact reaction and that the reaction is of first-order type. The log of the rate constants calculated from the slopes of the straight lines in Figs. 2 and 3, when plotted against $1/T$, do not give straight lines but lie on a curve whose slope increases with rising temperature. Similar curves are obtained from the B_1 and B_2 mixtures (Fig. 5). The kinetic data, therefore, do not seem to lead to a solution of the physical mechanism of the reaction. These data, however, do add some support to the chemical interpretation. The fact that two straight lines are obtained for the B_2 mixture at 792°C. indicates that a secondary process has taken control of the reaction rate after 70% of reaction. Chemical analysis shows that the orthosilicate is the main final product. The final slope in the log $(1 - \alpha)/t$ curve could be the result of the rate of formation of the orthosilicate. The increasing slopes of the log K vs. $1/T$ curves with rising temperature also suggest that a process with higher activation energy is involved in the reactions at higher temperatures, which agrees with the idea

[9] C. A. Snell and R. Ward, "Reactions in Solid State: Reaction Between Monazite and Sodium Carbonate," in publication.

that the $Si_2O_7^{-6}$ and $Si_3O_{10}^{-8}$ ions are reacting to an increasing degree with the carbonate ion to form the orthosilicate.

IV. Summary

The reactions of sodium carbonate and quartz have been investigated between 726 °C. and 805 °C. Mixtures of different composition and containing uniform and nonuniform silica particles were used. Various factors involved in the measurement of rates of reaction using the flow method were investigated.

The size of charge, rate of flow of nitrogen, duration of reaction, and composition of the mixture have been shown to have appreciable influence on the reaction rates and on the composition of the product. A theory of the formation of silicate ions has also been proposed. Although the rate data lend support to this theory, the mechanism of the reaction is not thus determined with certainty. For a complete picture of the reaction mechanism, it will be necessary to know the quantity of silica which has reacted at all times during the course of the reaction.

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Is the Only Workable Program

Federal and State Social Security Benevolences Are Desirable
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Hospitals, Homes, Asylums, and Pensions For Many Years Have
Been State and Federal Enterprises—But Only for the Helpless

Opportunities in Free Enterprise Await Self-Reliant Persons Who
Conserve Their Energies and Resources

ONLY BY RUGGED INDIVIDUALISM
HAVE NATIONS PROSPERED

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GREEK □ □ *KERAMOS—FIRED STUFF*

Ceramics Is Production by Action of Heat on Earthy Materials Which are Predominately Silica and Silicates

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Ceramic Technologists Compound Silicates Achieving Fired Products Having Prescribed Properties

Ceramic Engineers Mine and Beneficiate Silicates They Devise Methods and Equipment by Which Ceramic Products Are Economically Processed

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CERAMIC TECHNOLOGISTS PRACTICE IGNEOUS PHYSICAL CHEMISTRY

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Progressive Improvement in Ware Quality, Lowering of
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Require Continuous and Intensive Promotion of

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